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ASSESSING THE ROLE OF CLIMATE CHANGE AND LAND COVER CHANGE IN
ECO-HYDROLOGIC MODELING

(SNOWMELT TIMING AND DISSOLVED ORGANIC CARBON FLUXES)

A Dissertation Presented

by

SHABNAM ROUHANI

Submitted to the Office of Graduate Studies,
University of Massachusetts Boston,
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

May 2018

Environmental Sciences Program

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ABSTRACT

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May 2018

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This study explores temporal trends in snowmelt timing, dissolved organic carbon (DOC) concentrations, and DOC fluxes in the large forested Penobscot watershed of Maine. The spatially-distributed process-based Regional Hydro-Ecological Simulation System (RHESSys) model was used to simulate streamflows and DOC fluxes and concentrations from 2004-2013 with peak transport generally associated with snowmelt. Results were evaluated with field measurements (streamflow, DOC concentrations and fluxes) and remotely sensed products (Net Primary Production (NPP) and Leaf Area Index (LAI)). The annual and inter annual variability in the amount of fluvial DOC export was further explored under future climate change scenarios and predicted land cover compositions of the watershed.

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LIST OF ABBREVIATIONS

API	antecedent precipitation index
DEM	digital elevation map
DHSVM	distributed hydrology soils and vegetation model
DOC	dissolved organic carbon
DOM	dissolved organic matter
DON	dissolved organic nitrogen
FI	feedback index
GLUE	generalized likelihood uncertainty estimation
GPP	gross primary production
IPCC	Intergovernmental Panel on Climate Change
LAI	leaf area index
MODIS	moderate resolution imaging spectroradiometer
NLCD	national land covers dataset
PI	Precipitation index
RHESSys	regional hydro-ecological simulation system
TI	Temperature index
USGS	united states geological survey
USGRCP	United States global change research program

CHAPTER 1

INTRODUCTION

Overview

Snowmelt provides a significant proportion of the volume of water that enters river systems. During certain times of the year, water from snowmelt can be responsible for almost all of the streamflow in a river. So, a lack of water stored as snowpack in winter can affect the availability of water for the rest of the year and impact downstream reservoirs. The northeast USA has experienced noticeable changes in climate since 1970 (with a rise in annual temperature of 2°F and an increase of 4°F in winter temperature). Furthermore, changes in form of winter precipitation (rain rather than snow) have also been detected. These recent changes in winter temperature and the form of precipitation have resulted in a reduction in snowpack and earlier spring snowmelt times leading to earlier peak flows (Betts, 2011).

Average temperatures in New England have risen during the 20th century, especially during the winter months (Hayhoe et al., 2007). “The response and magnitude of streamflow events to warmer winters may be significant, because a major component of the hydrology of river basins in New England is related to snowpack and the timing of snowmelt” (Dudley and Hodgkins, 2002).

The New England region is characterized with large spatial variation in the influence of climate because of the mountainous topography, coastal orientation, position to North American continent and storm tracks. The specific climate characteristics of New England (cold winter and high winter precipitation), makes this region sensitive to changes in climate variables such as temperature and precipitation. The time, magnitude, and form of winter precipitation all directly influence the timing and magnitude of hydrological cycles in an ecosystem.

In addition to the above climate changes, the land covers that comprise a watershed have also been changing, affecting the nutrients and matter entering streams. New England's landscape is dominated by natural forest and it is sparsely populated. It provides important ecosystem services such as buffering shorelines, protecting water supplies and sequestering carbon in soil and vegetation. However, as a result of climate change or land cover change this balance might be altered in future. Longer growing seasons, altered natural ecosystems, and shifts in terrestrial carbon cycle and storage are some of the current changes that have already impacted ecological cycles in the New England region. (Alan K Betts, 2011). Dissolved organic carbon (DOC) is an important component of the carbon cycle, leaching DOC from terrestrial land covers into the stream flow of a watershed, and eventually serving as a large source of marine DOC. The importance of DOC lies in its role to hydrological transport of carbon between terrestrial carbon pools into soil pools and eventually into streams.

In large heterogeneous catchments, stream DOC dynamics are regulated by the combined effects of hydrological mechanisms and the proportion of major landscape elements, such as wetland and forested areas. The Penobscot River basin in north-central Maine is the second largest watershed in New England, draining 22,400 km², nearly one-third of the State of Maine.

This research evaluates the response of streamflow and DOC flux to changes in the climate and land cover of the Penobscot Watershed by using the Regional Hydro-Ecological Simulation System (RHESSys) model. Remotely sensed data and field measurements of streamflow and streamflow DOC are then used to evaluate the modeled results. RHESSys is also of use in exploring future climate change and land cover change scenarios through variations in the model parameters (land cover types, anthropogenic development, deforestation, changes in climate status etc.).

In this work, a special emphasis has been placed on the effects of climate change on snowmelt timing and DOC flux within the Penobscot Watershed and the possible response to future changes in the extent of forested and wetland areas in the watershed. Temporal trends in snowmelt timing as a result of climate change projections, as well as changes in the amount of DOC export under both climate change projections and land cover change (forest vegetation shifts and wetland loss), have all been modeled for the Penobscot Watershed.

1.1. Research Area

The Penobscot Watershed:

The Penobscot River basin (figure 1.1) in north-central Maine is the second largest watershed in New England, draining about 22,400 km², nearly one-third of the State of Maine.

The West Branch of the Penobscot River rises near Penobscot Lake on the Maine/Quebec border; the East Branch begins at East Branch Pond near the headwaters of the Allagash River, and the main stem empties into Penobscot Bay near the town of Bucksport.

Despite its size, the watershed has a low human population density and is mostly forested

(red maple, spruce, sugar maple, yellow birch, and white pine), with extensive bogs, marshes, and wooded swamps covered in shrubs, low vegetation and bare soil (Griffith and Alerich, 1996; Anderson, 1996). The Penobscot watershed also has many large lakes and cold water tributaries which make it a suitable environment for important native fisheries such as the Atlantic salmon and brook trout.

The Penobscot Watershed is mostly well drained and has acidic soils which contain organic matter with a low decomposition rate. Precipitation is distributed rather uniformly throughout the year and the Watershed has a mean annual temperature of 4.87 C (40.7 F).

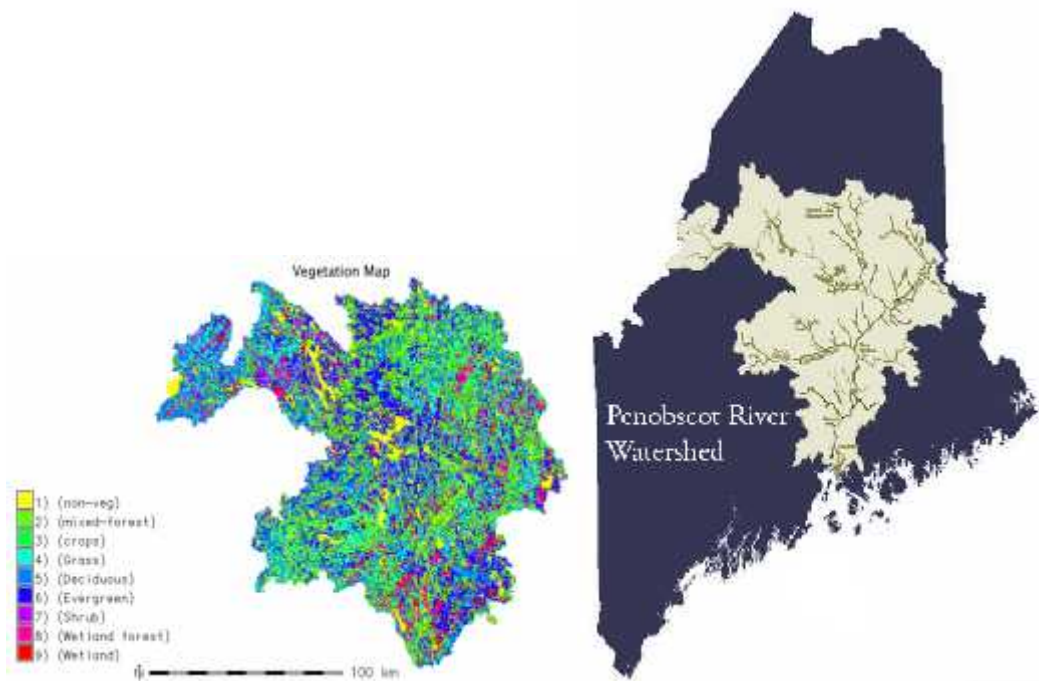


Figure 1.1, The Penobscot Watershed in State of Maine

1.2. The Regional Hydro-Ecological Simulation System (RHESSys)

Remote sensing and *in situ* data can both be used as inputs to simulate watershed dynamics using complex land surface models (e.g. TOPS and the Regional Hydro- Ecological Simulation System (RHESSys) (Nemani et al.,2009; Tague and Band 2004). RHESSys has an internal structure that defines the hierarchical representation of the landscape, and combines several different process models, to make it possible to study fluxes at different scales. There are five different spatial scales in this model (basins, hillslopes, zones, patches and canopy strata.

The basin defines the drainage area as a single stream network and defines the largest scale, and the areas that drain one side of a stream slope are defined as the hillslope. At the zone level, areas with similar climate forcing conditions can be defined, and patches (the finest spatial units in RHESSys) are the areas having similar soil moisture and land use characteristics. The canopy in RHESSys is represented by a strata of vertical layers. Each level of spatial hierarchy defined in the RHESSys mode, covers the next level. For instance, basins embed hillslope , hillslope cover zone level and zone levels fully covers strata and patch levels.

A set of state and flux variables along with processes representations (mathematical equations) and model parameters are used in RHESSys model. Each spatial unit within the catchment scale is associated to specific processes modeled by RHESSys. For instance, atmospheric flux estimation such as radiation is set to be modeled at zone level. Ecological processes such as photosynthesis, transpiration are associated at strata level while soil moisture redistribution processes is defined at patch level. A text document called a worldfile is then used to reference input maps with typical vegetation, soil and land cover characteristics of the study area for initialization state variables representing landscape at watershed scale. And a flowtable

describe the connectivity between the patches which are the smallest scale (500m * 500m) in this study. This information is then used in RHESSys using hydrological models embedded in RHESSys model to model subsurface and overland flow routing.

The MTN-Clim model (Runnig et al., 1987) is another sub-model in RHESSys that uses topography and climate saturation variables to model climate variable over spatially varying terrain. An ecophysiological model based on BIOME-BGC (Runnig and Coughlan, 1988; Running and Hunt, 1993) is also used to model carbon, water and nutrient fluxes at the canopy cover scale.

As mentioned previously, RHESSys has also already been successfully applied to some New England watersheds (although none so large as the Penobscot). It has been applied to the urbanized Neponset Watershed located to the south of the city of Boston, Massachusetts to simulate DOC flux into Boston Harbor (Yang et al., 2014). Kim (2015) also investigated the influence of mixed plant landscapes on eddy-covariance flux data by using the RHESSys model to study the influence of climate variability and insect infestation on a mixed forest at the Harvard Forest Long Term Ecological Research site in central Massachusetts. Figure 1.2, summarizes RHESSys framework with respect to input data to outputs.

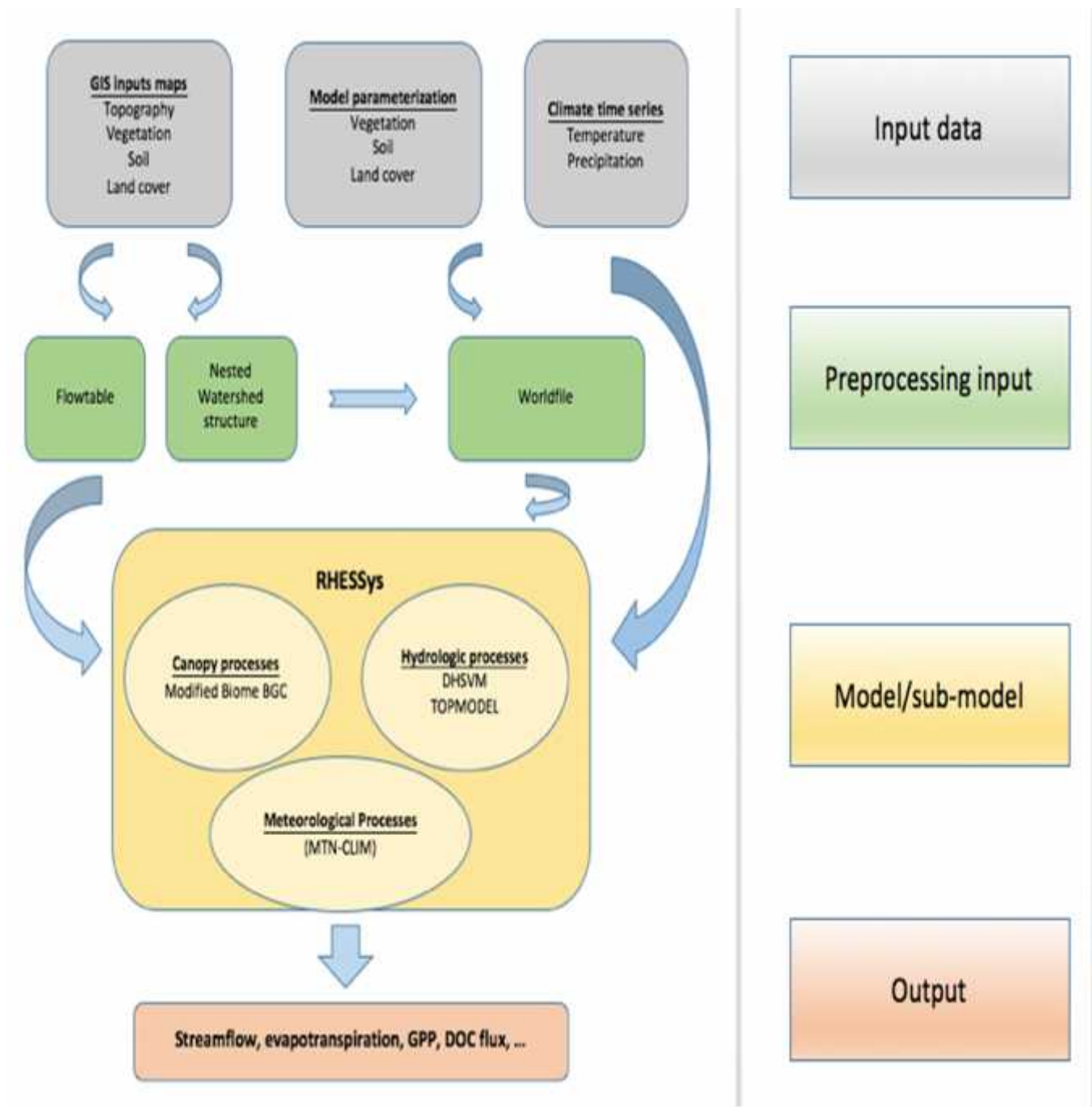


Figure 1.2, RHESSys framework

1.3. Snowmelt timing

Streamflow represents the integrated response of a drainage basin to climatic variables, especially precipitation and temperature. The northeast USA has already experienced a noticeable change in climate since 1970 (with a rise in annual temperature of 2°F (1.1°C) , and an increase of 4°F (2.2°C) in winter temperature, and an increase in precipitation of approximately five inches).

Worldwide, increased global temperatures have been associated with accelerating losses in sea ice, glacial mass balances, permafrost, and snow cover extent and duration (Serrez et al., 2009).

Based on the Intergovernmental Panel on Climate Change (IPCC) Assessment Report 5 (AR5 = IPCC, 2014), annual and seasonal temperatures and precipitation increases should be expected in the future under both the low and high emission scenarios (IPCC (2014): Climate Change 2014, North America. Chapter 26). Average annual temperature across State of Maine has increased by about 3.0 °F (1.7 °C) and total annual precipitation has increased by six inches (15 cm) between 1895 and 2014 (U.S. Climate Divisional Dataset ncdc.noaa.gov/monitoring-references/maps/us-climate-divisions.php).

Hydrological processes in high elevations are particularly sensitive to changes in climate, as both precipitation and temperature can experience abrupt changes over short distances due to altitudinal gradients and differing exposures to radiation and winds (Beniston, 2005). Therefore, a study of the annual amount and the timing of peak river flows is a good indicator of climate-related changes, or lack of change.

A recent study done by the United States Geological Survey (USGS) has shown that the annual average streamflow has increased across Northeastern and Midwestern United States, although other regions have not experienced such noticeable changes (U.S. Geological Survey. 2016). Furthermore, they have shown that seven-day low flows have generally increased in the Northeastern and Midwestern United States, while low flows have decreased in the Southeastern and the Pacific parts over the past 75 years (U.S. Geological Survey. 2016).

Furthermore, monitoring of high springtime river flows has shown that these peak flows have been arriving one to two weeks earlier in large parts of northern New England during the 20th Century (Hodgkins et al., 2003; Hodgkins and Dudley, 2006).

The most important variables controlling the amount and timing of snowmelt are wind, relative humidity, radiative fluxes, energy advection, turbulent heat fluxes and temperature departures. (Groisman et al., 1994; Zhang et al.,1997; Aizen et al.,2000; Ohmura 2001). Many regions across the United States have experienced a decrease in the proportion of precipitation falling as snow that is more winter precipitation is falling in the form of rain instead of snow (National Oceanic and Atmospheric Administration, 2016).

Therefore, the amount and timing of runoff into rivers is directly affected by the amount, timing, and form of precipitation (rain, sleet, or snow), and spring snowmelt is the most important contribution to many rivers, especially in northern and mountainous areas of the New England region (Hodgkins and Dudley, 2006). Considering the potential increase in air temperature predicted for the future, this warming is expected to lead to a reduction in snow and will cause an earlier onset of snowmelt. Earlier snowmelt, on an annual basis, is therefore expected to result in consequences for some aquatic ecosystems and for human utilization of watershed flows.

Earlier spring time snowmelt has already been observed in many rivers across the United States (Stewart et al., 2004, Cayan et al., 2001). Trends toward earlier streamflow in northern New England are consistent with studies of earlier Ice-out dates in New England. Ice-out dates have become significantly earlier in New England since the 1800s. (Hodgkins et al., 2002) and have been shown to be strongly correlated to air temperature in the month or two months before melting (Tramoni et al., 1985; Palecki and Barry, 1986; Robertson et al., 1992; Livingstone, 1997). Therefore, a major component of the hydrology of river basins in New England involves snowpack and the timing of snowmelt and ice melt with more sensitivity to warmer winters (Dudley and Hodgkins, 2002).

While earlier snowmelt being caused by projected warming seems obvious, a better understanding of how snowmelt timing will respond to predicted climate change scenarios still needs more exploration. One of the objectives of this research is to assess the impact of potential climate change on snowmelt timing, by using the RHESSys model. In this research, we focused on modeling the impact of variations in snowmelt timing (and the dissolved organic carbon transport) for the Penobscot Watershed of Maine and explored the possible changes the watershed may experience moving forward by considering both the low and high emission scenarios predicted for the mid and end of the century.

1.4. Dissolved Organic Carbon (DOC) flux

The carbon, water, and nutrient cycles in terrestrial ecosystems are tightly linked together. The cycling, storage, and transport of carbon to marine systems has become a critical issue in global change science, especially with regards to the northern latitudes (Freeman et al., 2001; Benner et al., 2004). Soil organic carbon is a crucial carbon sink and is the source of the

largest portion of the carbon flux from the land (Schlesinger, 1997; Lettens et al., 2004; Kardjilov et al., 2006). Characterizing the ecosystem carbon fluxes and estimating the quantities of these fluxes at various scales (local, regional, continental and global) improves our understanding of the relationship between the terrestrial biosphere and the atmosphere and aquatic systems (Law et al., 2006; Xiao et al., 2010).

Two major pools of carbon in terrestrial ecosystems involve the long term storage of carbon in plants and wood through assimilation of atmospheric CO₂ into plant biomass, and plant turnover rates and decay cycles that result in storage of carbon into litter and soil pools.

Dissolved organic carbon (DOC), is an important component of this carbon cycle and represents the carbon that is leached from terrestrial watersheds into their streamflows to serve as a large source of DOC in nearshore marine environments.

The balance between terrestrial and aquatic primary production and decomposition controls the amount of DOC that is transported. Although, dissolved organic carbon fluxes are relatively small in relation to the carbon fluxes associated with primary productivity or heterotrophic respiration in terrestrial systems (Schimel, 1995), “the internal system DOC fluxes are much larger than the stream DOC fluxes especially in the northern latitudes where the transport of soluble carbon from the terrestrial system provides a substantial component of the ecosystem carbon cycle” (Neff et al., 2001).

Furthermore, vertical and lateral flows through soils are very important in soil formation. (McDowell and Wood 1984; Trumbore 1993). In addition, Dissolved Organic Matter (DOM), which includes both dissolved organic carbon and dissolved organic nitrogen, serves as a vector for the loss of carbon (C) and nitrogen (N) from terrestrial ecosystems. Therefore, long term

changes in DOM production can affect net primary productivity (Hedin et al.,1995; Vitousek et al.,1998).

Currie and Aber (1997) coupled a decomposition model (DocMod) with a hydrology model that predicts litter production and actual evapotranspiration, and applied this coupled model to the White Mountain National Forest. They found that conifer forests tend to have slower decay rate of humus than deciduous forests, and the forest floor predicted masses of organic matter were higher in spruce-fir forests than in hardwoods.

Aitkenhead and McDowell (2000) used the C:N ratio in soil as a predictor to estimate annual DOC flux at both local and global scales. They stated that mean soil C:N ratio of a biome accounts for 99.2% of the variance in annual riverine DOC flux among biomes at global scale. Their result on three test watersheds showed that the predicted flux of each watershed was within 4.5% of the actual DOC flux using C:N ratio as an indicator. A landscape-mixing model was also recently used to predict DOC concentrations from contributing landscape elements (Agren et al., 2013). They found that peat soils had the highest DOC concentrations, followed by till and lastly, fine sorted sediments. The SPARROW (SPATIally Referenced Regressions On Watershed attributes) empirical model was developed by the USGS specifically to predict mean annual loadings of nutrients using nonlinear regression equations (Schwarz et al., 2006) with *in situ* measurements and streamflow data for non-conservative transport. Also this model has been used for DOC simulations. The Load Estimator (LOADEST) regression software (Runkel et al.,2004) is another empirical model that relates point samples to an entire watershed as a function of the regression relationship using streamflow, time frame, and observed measurements (Huntington and Aiken, 2013).

In this study, RHESSys, a spatially distributed model that simulates carbon, water and energy fluxes within a watershed, is used. The ability to combine a process based model for vegetation growth, with the hydrological and decomposition models in RHESSys, makes it possible to study DOC fluxes between terrestrial and aquatic ecosystems. Furthermore, RHESSys is capable of modeling the spatio-temporal interactions between the different processes at the watershed scale.

RHESSys has been successfully applied in diverse watersheds under a number of different climate conditions (Shields and Tague 2012; Tague et al.,2004), and has been used to study nitrogen export (Band et al., 2001), investigate streamflow feedback due to climate change (Band et al.,1996; Baron et al.,2000; Tague and Grant,2009; Tague et al.,2007), parameterize ungauged watersheds (Tague et al.,2012), study hydrologic vegetation gradients (Hwang et al.,2012), investigate the eco-hydrologic response to the combined impacts of projected climate change and altered fire frequencies (Tague et al., 2009), and study the impacts of snow distribution (Christensen et al.,2008; Hartman et al., 1999; Tague and Grant,2009). RHESSys has also been successfully applied to the small urbanized Neponset Watershed, located to south of the city of Boston, Massachusetts, to simulate the DOC flux that exits this New England watershed and enters Boston Harbor (Yang et al., 2014).

In addition to the main river and tributaries, there are several lakes and reservoirs located in the Penobscot Watershed. Changes in climate variable such as temperature and precipitation have already been shifting the timing of snowmelt and ice-out towards earlier dates. Therefore, an advance in the timing of snowmelt runoff may increase the length of summer droughts with important consequences for the water supply of an ecosystem. In summary, the Penobscot watershed has a large impact on the hydrology of northern New England, making it an important

region to use to study temporal trends in snowmelt timing, and DOC flux and DOC concentrations, as they move from a forested watershed into a marine ecosystem. Thus it is also an ideal watershed to use to investigate how these trends will change according to future climate change projections.

1.5. Land cover change scenarios and DOC fluxes and concentrations

Runoff, slope, soil organic matter, and land cover characteristics (vegetation type and existence of wetlands and lakes in the catchment) are the main spatial factors controlling the variability of fluvial Dissolved Organic Carbon (DOC) fluxes through the catchment. Strohmeier et al., 2013 has reported that DOC export in runoff originates mainly from the wetland areas of a catchment. Findlay et al., 2001 has concluded that land use can affect both the quantity and quality of DOC exported into rivers from surrounding terrestrial sources.

In this study, we have utilized changing scenarios of land cover and investigated how these can affect DOC fluxes and concentration. In large heterogeneous catchments such as the Penobscot, the stream water DOC dynamics are regulated by the combined effects of hydrological mechanisms and the proportion of the major landscape elements, such as wetland and forested areas.

Forest:

This study therefore also focused on projected changes in forested and wetland extent. Projected increases in atmospheric CO₂ concentration and changes in temperature and precipitation patterns have the potential to alter ecosystem functions, species interactions, population biology, and plant distribution (Melillo et al., 1990; Kirschbaum, 2000). An earlier study on projections of land use change in the State of Maine (Plantinga et al., 1999) had

suggested a three percent decline in forested area from 2000 to 2050. This study is in general agreement with the newest release of the National Climate Assessment (2014) which has predicted an approximately two percent decline in forested areas in the Northeastern US from 2000 to 2050. Interestingly, a comparison of the 2001 with the 2011 State of Maine land cover maps (NLCD, USGS) depicts an increase in conifer trees, especially in the northwest and western part of the State, and a loss in both mixed and deciduous forests in the southern half of the State. Furthermore, in the southern half of the State, deciduous and mixed forest have been replaced by either grasslands/shrublands or herbaceous plants. In another study (Rustad et al., 2014) on North American forest and Eastern Canada, a reduction in suitable habitat for Conifer forest and an expansion of Deciduous forests was reported. In this study, we were interested into exploring the role of forest species composition on DOC flux and concentration. Different vegetation types will have different effects on fluvial DOC export by influencing hydrological cycles as well as impacting productivity rate and decomposition processes. For this reason, it is worth looking at the effects of possible future changes in forest extent and in changes in vegetation type distributions on the fluvial DOC. Four extreme vegetation change scenarios have been considered, which estimate that climate change and land cover changes will result in either the relative dominance of coniferous or deciduous vegetation types in the forested areas of the future.

The Penobscot Watershed's forest vegetation types are an assemblage of mixed forest (conifer and deciduous), conifer, and deciduous types. Table 1.1, represents the various progressive land cover changes for the above land cover change scenarios. For the first scenario, resulting in a coniferous vegetation type dominance in the future, a progressive land cover change has been used in that the extent of current coniferous areas will remain coniferous,

deciduous areas will be converted to mixed forest, and current mixed forest areas will be replaced by primarily coniferous types. In the second more extreme scenario, following the first scenario, all the forest type vegetation will be converted to conifers (100% conifers). Other progressive land cover changes for the third and fourth scenarios move the forested areas toward more of deciduous type dominance. For the third scenario, current coniferous areas will be replaced by mixed forest types and current mixed forest types will be replaced by deciduous types, while deciduous areas will remain constant. In the fourth scenario, following the third scenario, all the forest type vegetation will be replaced by deciduous trees (100% deciduous). These various land cover studies can be used to better understand the role of vegetation types in fluvial DOC export.

Table 1.1. Progressive forest vegetation composition change

Forest vegetation Types (Original)	Conifer Dominancy		Deciduous Dominancy	
	Mixed-Conifer	Conifer	Mixed-Deciduous	Deciduous
Conifer	Conifer	Conifer	Mixed	Deciduous
Deciduous	Mixed	Conifer	Deciduous	Deciduous
Mixed	Conifer	Conifer	Deciduous	Deciduous

Wetlands:

The DOC flux from watersheds containing significant wetlands also needs to be addressed when performing a carbon mass balance. Therefore, as a second approach of looking at possible future changes in the amount of fluvial DOC export from the Penobscot Watershed into the Gulf of Maine, we investigated the impact of wetland loss, as a result of climate change,

on the amount of fluvial DOC export. A number of studies have demonstrated that the extent of wetlands, especially peatlands, controls the watershed level transport of DOC in streams (e.g. Gergel et al., 1999, Kolka et al., 1999). Global climate change is recognized as a threat to species survival and the health of these wetland systems, as they are particularly vulnerable to changes in the quantity and quality of their water supply, and to changes in their hydrological regimes. Therefore, climate change is expected to affect the hydrology of individual wetland ecosystems through highly variable changes in precipitation and temperature.

In this research, we explore the role of wetlands in the fluvial export of DOC from Penobscot Watershed into the Gulf of Maine by manipulating wetland abundance based on an input wetland map created from a wetness index and elevation.

Previous studies done by the USGS have shown a slight decrease in wetland extent in the eastern half of the state of Maine for the time period of 1973 to 2000 (0.1%) while no change was reported for the western half of the State during this period (Sayler et al., 2016). A comparison of the 2001 and 2011 land cover maps shows a slight overall decrease in wetland areas. Unfortunately, there is no specific information available for predictions of future changes in the amount of wetlands in all of New England as a result of climate change. However, there is a possibility that some proportion of wetland areas in the region will be lost due to an overall drying trend in the future (Feng and Fu, 2013; Sherwood and Fu, 2014). For this reason, we explored the impact of a range of wetland losses across the watershed to study the resultant changes that may occur in the annual amount of DOC export from the Penobscot Watershed.

Therefore, an incremental increase in the loss of wetland areas was implemented in this study to explore the sensitivity of watershed to large wetland losses. Exploring incremental changes in the loss of wetland areas will help us to understand the role of wetlands in carbon

cycling in the catchment. We then used a second explicit approach to look at the impact of wetland loss on the amount of DOC flux by using ARC GIS as a tool to shrink wetland areas by one and two pixels. One pixel in our study covers 500m by 500m area. More information about the methodology can be found in chapter four.

This effort is focused on the realistic modeling of the Penobscot Watershed, Maine to capture the current impacts of snowmelt timing and land cover distributions on DOC concentrations and fluxes into the Gulf of Maine. The RHESSys Model is also used to estimate the impact of predicted climate change scenarios, with associated changes in the future distribution of forested land covers and wetland extent. In Chapter two, we focused on the use of RHESSys model to assess the impact of climate change on snowmelt timing. Chapter three was then followed by RHESSys simulation of DOC flux and DOC concentration in the Penobscot Watershed and exploring the climate change impact on both DOC flux and concentration while in chapter four the role of wetland and forest vegetation composition were assessed.

CHAPTER 2

EVALUATING TEMPORAL TRENDS IN SNOWMELT TIMING BASED ON FUTURE CLIMATE CHANGE SCENARIOS

2.1. Introduction

Snow accumulation and melt dominate the hydrologic cycle of the watersheds in the mountainous and high latitude areas of the northern continental US. Snowpack acts as a natural water storage system, providing runoff to aquatic and riparian ecosystems, reservoirs, and agricultural lands. The study of snow hydrology has evolved greatly over the past 60 years, from the first report on Snow Hydrology (U.S. Army Corps of Engineers, 1956). The importance of snow accumulation and subsequent melting processes has led to significant research in snowmelt modeling. “The physical processes within a snowpack are highly complex. Consideration of mass and energy balance, mass transport by conduction, vapor diffusion and meltwater drainage are needed “(Tarboton and Luce, 1996).

Many models dealing with snow accumulation and snowmelt have been developed (Martinec, 1960; Anderson, 1968; Rango and Martinec, 1970; Blöschl et al., 1991; Jordan, 1991; Martinec et al., 1994; Garen and Marks, 1996; Coughlan and Running, 1997, Mitchell and Dewalle, 1998; Tague and Band, 2004). Models range from complex energy balance models to more simplistic degree day based models. Available models dealing with snow accumulation and

snowmelt include the precipitation-runoff modeling system (PRMS), the Variable Infiltration Capacity (VIC), the Snowmelt Runoff Model (SRM), the Soil Water Assessment Tool (SWAT), and the Regional Hydro-Ecologic Simulation System (RHESSys) which has been used in this study.

PRMS explores the impacts of various combinations of precipitation, climate, and land use on streamflow, sediment yields, and general basin hydrology (Leavesley et al., 1983). The VIC model (Wood et al., 1992) simulates macro scale spatial variability of infiltration and runoff. VIC has been used for long term water supply and flood. The Snowmelt Runoff Model (SRM) is being used for simulation of snowmelt in mountainous areas using a conceptually based, temperature index model (Martinec et al., 1994; Mitchell and Dewalle, 1998). The SWAT Model is a basin scale, continuous-time model that is designed to investigate the impacts of sediment and water management and agricultural chemical yields in ungauged watersheds. (Arnold et al., 1998; Arnold and Fohrer, 2005).

RHESSys is a GIS based hydro-ecological model that has been used for carbon, water and nutrient fluxes simulation (Tague and Band, 2004) and is the model used in this research. RHESSys has been used for transpiration simulation (Christensen et al., 2008), exploring climate change impact on water yield (Zierl and Bugmann, 2005) and simulation of snow distribution, especially in mountainous watersheds (Hartman et al., 1999), amongst other applications. Two distributed hydrologic models (TOPMODEL and DHSVM (Distributed Hydrology Soil Vegetation Model)) are used as sub-models within RHESSys for vertical and lateral fluxes including soil moisture distribution and runoff production. RHESSys uses sublimation, radiation, temperature and precipitation driven melt to calculate snowmelt and to compute Snow water equivalent (SWE) and snowpack changes. Energy balance and mass balance approaches are used

respectively to estimate snowmelt and accumulation within the watershed. Also, RHESSys considers snowmelt and accumulation from vegetation canopy covers by considering specific snow interception capacity and litter and detention storage on the forest floor. More detail about streamflow, snowmelt and accumulation procedure within RHESSys is described in the methodology section in this chapter. More details about RHESSys is also available at (Tague et al., 2004).

The flow of a river represents the entire basin response to various climatic inputs, with precipitation and temperature being more important than other variables. Thus any changes in the climatic variables involved in the water cycle may alter the hydrological regimes. A warmer climate may result in more precipitation falling as rain, an earlier snowmelt runoff, and eventual limits to water storage and runoff during the dry season. Increasing temperatures may also affect evapotranspiration rates and, in snow-dominated mountainous regions, can have a large impact on the amount of accumulated snow and on the timing of the snow accumulation and melt, leading to a further alteration of hydrological regimes (López-Moreno and García-Ruiz, 2004; Tague and Peng, 2013).

Substantial research has been carried out in the field of hydrology in order to predict the future behavior of various river flows under changing environmental conditions, especially climate variables and land cover distribution. In this effort, we focus on the eco-hydrologic modeling of the Penobscot, the second largest watershed in New England, in order to explore the impact that changes in the timing of snowmelt will have on the streamflow.

Many researchers have demonstrated the value of using historical river flows as climatic indicators and have studied temporal changes in river flow (Hyvarinen and Leppajarvi, 1989; Lettenmaier et al., 1994; Lins and Michaels, 1994; Chiew and McMahon, 1996; Lins and Slack,

1999; Dettinger and Diaz, 2000; Douglas et al., 2000; Zhang et al., 2001; Burn and Hag Elnur, 2002; McCabe and Wolock, 2002). National and regional studies have also looked at seasonal changes in river flows by using the ratio of seasonal to annual flows (Aguado et al., 1992; Dettinger and Cayan, 1995), the magnitude of monthly flows (Lettenmaier et al., 1994; Zhang et al., 2001; Burn and Hag Elnur, 2002), and temporal changes in seasonal peak flows (Burn, 1994; Cayan et al., 2001; Zhang et al., 2001).

The U.S. Geological Survey (USGS) has documented many seasonal climate-related changes in the northeastern United States that have occurred during the last 30 to 150 years. Earlier snowmelt runoff in the late winter and early spring, decreasing ice-on-lake duration time, decreasing number of days of ice-affected flow, reductions in the amount of snowfall to total precipitation, and denser and thinner late winter snowpack are all strongly correlated with warming winter and spring air temperatures (Hodgkins et al., 2003a, 2003b; Hodgkins et al., 2002; Huntington et al., 2004; Hodgkins and Dudley, 2006).

Therefore, climate model projections for the Northeast indicate rises in air temperature and annual evaporation, decreases in annual water yields, and earlier snowmelt runoff times (Hayhoe et al., 2007). Many studies have already documented earlier snowmelt, a shift to earlier streamflow timing, altered spring maximum flows, and/or intensified summer droughts (Barnett et al., 2008; Burakowski et al., 2008; Brabets and Walvoord, 2009; Adam et al., 2009; Burn et al., 2010; Cuo et al., 2009; Hamlet et al., 2007; Hodgekins et al., 2003a; Hodgekins and Dudley, 2006; Huntington et al., 2004; Jefferson et al., 2008; Knowles et al., 2006; Lee et al., 2004; Mote et al., 2003; Shepherd et al., 2010; Stewart et al., 2005; Stewart, 2009; Wilson et al., 2010; Xu et al., 2009).

Current changes in winter/spring streamflow can be explained by warmer temperature that may also cause a reduction in the ratio of winter precipitation falling as snow, which in turn contributes to the earlier melting of snowpack. Such a switch in the state of precipitation not only alters the timing of intra-annual runoff but also tends to yield less total annual runoff. “A decrease in snowfall amount combined by an increase in temperature, can lead to an earlier spring peak river runoff and a reduction in summer and autumn runoff for a given total annual precipitation” (Zhang et al., 2015).

The climate characteristics of New England rivers, such as near-freezing temperatures present in the late fall, winter, and early spring, make these rivers sensitive to small changes in temperature. Moreover, the relative amount of precipitation falling as rain or snow also directly affects the timing of river flow in these seasons, as the largest river flows in New England typically occur in the spring when rain runoff from snowpack or from saturated soils is the greatest.

2.2. Data and Methodology

2.2.1. Model inputs

The Global Historical Climatology Network (GHCN) is an integrated database of daily climate summaries from global land surface stations. The GHCN-Daily source data have been obtained from the National Meteorological and Hydrological Centers (NMHCs) located around the world. The U.S. Collection contains daily data from a dozen separate datasets and is archived at NOAA/NCDC. In this study, climatic data (daily precipitation and minimum and maximum temperatures) for the two periods of 1963–1980 and 2000–2014 were obtained from the National Climatic Data Center (NCDC, NOAA).

Hydrological data, used for calibration and validation purposes, were provided by U.S. Geological Survey (USGS) (<http://www.usgs.gov/water/>). Daily streamflow data at the somewhat inland west Enfield gauge station were downloaded from the United States Geological Survey (USGS) for the period of 2000-2013. The daily discharge was then estimated using an area adjustment to the discharge measured for the Penobscot River at Eddington (the actual mouth of the Penobscot). This method of estimation has already been used in another study (Huntington and Aiken. 2013) where the export of dissolved organic carbon from the Penobscot River basin was modeled using the same observational DOC data and the coarser resolution empirical LOADEST model. The remotely sensed data used in this study are land cover, soil type, leaf area index (LAI), and a digital elevation model (DEM).

The DEM data for the State of Maine was downloaded from National Elevation Dataset (NED) on the United States Geological Survey (USGS) website. In this study, 500-meter resolution data is used, scaling up from the 30-meter elevation data downloaded from the National Map viewer website. The nearest neighbor resampling technique was used in Arc GIS for scaling up 30m resolution to 500m resolution. The 500m resolution was chosen in this study because of the large scale of the Penobscot Watershed and the ability to compare RHESSys simulated results with satellite derived MODIS products for evaluations.

Land cover data were also downloaded from the USGS website, via the National map viewer (<http://viewer.nationalmap.gov/viewer/>). The version used in this research is NLCD (the National Land Cover Data) 2006 with 17 land type categories. In this study, land cover data is then reclassified to 5 types (undeveloped, high intensity urban area, medium intensity urban area, low intensity urban area and agriculture) to match the RHESSys defined classification.

The 30-meter resolution land cover data was downloaded and then resampled to 500 meters. The nearest neighbor approach was used in Arc GIS resampling tool.

The Vegetation data were also derived from the NLCD 2006. The 9 categories used in this study, match the RHESSys defined vegetation classification types (un-vegetated, mixed forest, crops, grass, deciduous, evergreen, shrub, wetland and wetland forest).

The 30-meter resolution vegetation data were downloaded and then resampled to 500 meters. In addition, Leaf Area Index (LAI) information was used. Leaf Area Index is defined as the one-sided green leaf area per unit ground area in broadleaf canopies and as the one-half the total needle surface area per unit ground area in coniferous canopies. Generally, LAI is used to calculate surface photosynthesis, evapotranspiration, and net primary production. The MCD15A2H satellite product, derived from combined Terra and Aqua MODerate resolution Imaging Spectroradiometer (MODIS) data, was used in this study with a 500-meter resolution.

Other inputs data such as slope, aspect, drainage, and wetness index map were created from the DEM map using GRASS6.4. The stream network is created from the drainage map. The 30-meter resolution road map was also downloaded from USGS website. The impervious map was created from the road map and scaled up to a 500-meter resolution for this study.

In addition to climate time series data and GIS-based inputs, a library of commonly used parameter files were also assembled from an extensive literature search of field measurements and specific soil, vegetation, and land use types were assigned. Table 2.1, summarize the RHESSys input data and sources in this study.

Table 2.1, RHESSys input data

Data	Source
Climate data	National Climatic Data Center (NCDC)
Streamflow	U.S. Geological Survey (USGS)
Digital elevation map	National Elevation Dataset (NED)
Land cover map	National map viewer/USGS
Vegetation map	National map viewer/USGS
Soil map	Soil survey geographic database (SSURGO)
Slope, aspect, drainage map	derived from DEM map
Leaf Area Index	MODIS /MCD15A2H satellite product
Wetness index map	derived from DEM map
Road map	National map viewer/USGS
Impervious map	derived from road map

2.2.2. Spin up, calibration and validation

After a spin-up process, which involved running the model for a certain number of years to allow carbon and nitrogen stores to stabilize, and to build up an organic soil layer within the model simulation, the United States Geological Survey (USGS) stream gauge records were used to calibrate the model for the four independent parameters in RHESSys. These parameters include the hydraulic conductivity at the surface (Ksat_0), the decay of hydraulic conductivity with depth (m), and two groundwater parameters (the first of which controls the proportion of infiltrated water that bypasses the soil to reach a deeper groundwater table (gw1), and the second of which controls the rate of lateral flow from a hillslope scale groundwater table to the stream channel (gw2). The calibration effort first used a Monte Carlo sampling method to run the model over a range of values for Ksat_0 (0.1- 600) , m (0.1- 20) , gw1 (0.001 – 3) and gw2 (0.01 – 0.9).

The best fits were then used for further evaluations using the state of chain approach introduced by Markov chain. Due to the very large watershed area encompassed by the Penobscot (the largest watershed attempted to be modeled with RHESSys), the state of the chain was used as a sample of the desired distribution. The quality of the correspondence of the calibrated parameters improves as they approach the desired distribution of the calibrated parameters best fit for our study area. Therefore, the optimal correspondence calibrated values from the Highest-Nash-Sutcliffe (Nash and Sutcliffe 1970) and the best r-squared measures between observed and modeled streamflow were selected for future runs. The RHESSys model was then used to simulate streamflow for the period from 01/01/2000 to 12/31/2003 for calibration and then from 01/01/2004 to 12/31/2012 for validation.

2.2.3. Rain/Snow partitioning

The form of precipitation which occurs is particularly important in the practical consideration of snow hydrology. Direct observation of the form of precipitation is limited at most of meteorological stations, necessitating the use of indirect methods for estimating precipitation partitioning. Snowfall time series can be directly used in RHESSys. However, if this is not available, then a linear transition from snow to rain across a temperature range, defined by T_{min_rain} (minimum temperature at which rain can occur) and T_{max_snow} (maximum temperature at which snow can occur), is used to partition precipitation into rain and snow. A mix of rain and snow are considered between these two threshold temperatures. These variables are embedded in the zone default file in RHESSys. Precipitation partitioning in RHESSys is estimated through these stages, when average temperature is higher than maximum temperature than can snow, precipitation falls as rainfall and when average temperature is lower than minimum temperature that can rain, precipitation falls as snow:

$$T_{ave} = T_{max_snow} | \text{rainfall}$$

$$T_{ave} = T_{min_rain} | \text{snowfall}$$

RHESSy's original methodology for partitioning precipitation into rain and snow is based on the U.S Army Corps of Engineers (1956) Snow Hydrology which uses a min/max to obtain the range in which there is a mix of snow and rain. That study demonstrated that surface air temperature is as reliable as any other of the variables tested for differentiating between rain and snow. RHESSys uses a double threshold, with a lower threshold to define the minimum temperature that rain can occur (T_{min_rain}) (thus all precipitation below this threshold is defined as snow). An upper threshold is used to define the maximum temperature under which snow can fall (T_{max_snow}) (and thus all precipitation above this threshold is considered rain). In addition, the range between these thresholds is then considered to be mixed precipitation and is proportional to a linear regression between the defined thresholds.

Careful model parameterization for precipitation intensity, duration, amount, and precipitation form is needed in order to have a reliable estimation and prediction in cold regions (Gray, 1970). The uncertainty of these predictions is strongly influenced by the quality of the input data (Zehe et al., 2005) and the determination of an accurate precipitation phase. Therefore, in this research two methodologies for precipitation phase partitioning were used and the results were compared. We investigated another method of precipitation partitioning which incorporated more climate variables than just the surface air temperature which is the primary variable used in the RHESSys model. This methodology was developed by Dingman et al., (2014), and considers station elevation, wet bulb temperature, and humidity. More details about this methodology can be found in Dingman et al., 2014.

Wet-bulb temperature, T_{wb} (°C), is calculated as;

$$T_{wb} = T_a - \frac{e(T_a) * (1 - RH)}{\Delta(T_a) + 0.00066 * P(Z)} \quad (\text{Equation 2.1})$$

Where T_a is daily average temperature (°C), RH is relative humidity and $e(T_a)$ is saturation vapor pressure (KPa), given by;

$$e(T) = 0.611 * \exp\left(\frac{17.625 * T}{T + 243.04}\right) \quad (\text{Equation 2.2})$$

$\Delta(T_a)$ is the slope of $e(T_a)$ (KPa/°C), given by;

$$\Delta(T_a) = \left[\frac{2.1714}{(T + 243.04)^2} \right] * \exp\left[\frac{17.625 * T}{T + 243.04} \right] \quad (\text{Equation 2.3})$$

And $P(z)$ is atmospheric pressure (KPa), given by;

$$P(z) = 101.3 * \exp(-0.00013 * Z) \quad (\text{Equation 2.4})$$

The next steps calculate the parameter T_0 that is empirically related to elevation (z) and relative humidity (RH).

$$T_0 = -5.87 - (1.042 * 10^{-4}) * Z + (8.85 * 10^{-8}) Z^2 + (16.06 * RH) - (9.614 * RH^2) \quad (\text{Equation 2.5})$$

Then the threshold temperature is calculated for snow, rain, and a mix of rain and snow;

$$T_{min} = \begin{cases} (T_0 + 11.756) - (23.1 * RH) & \text{if } RH > 0.78 \\ T_0 & \text{if } RH \leq 0.78 \end{cases}$$

$$T_{max} = \begin{cases} 2 * T_0 - T_{min} & \text{if } RH > 0.78 \\ T_0 & \text{if } RH \leq 0.78 \end{cases}$$

Finally, the precipitation type is determined following the steps below;

$$T_{wb} \leq T_{min} \mid \text{Snowfall}$$

$$T_{min} < T_{wb} < T_{max} \mid \text{mix of rain and snow}$$

$$T_{max} \leq T_{wb} \mid \text{Rainfall}$$

2.2.4. Snow accumulation and melt

Various approaches to modeling snowmelt exist which are based on available data, and site characteristics such as Degree-Days, Temperature Index, and Energy Balance methods. The Degree Day method is a daily snowmelt approach to determine the average melt rate and the amount of melt water. The Temperature Index approach is an extension of the Degree Day method which calculates the change in the amount of melt water at each time interval based on an air temperature above a critical threshold. The Energy and Mass Balance methods are physically based approaches that calculate the amount of snowmelt by considering the energy transport between the snow and the surrounding air.

The mass balance equations address the snow accumulation and ablation processes, as well as the transformation of the snow water equivalent and snowpack water yield (Wigmosta, 2002). Radiation, temperature, precipitation and advection melt are all considered in the snowmelt modeling performed by RHESSys. Snowmelt is computed using a quasi-energy budget approach. Snowmelt due to latent and sensible heat flux is based on an empirical relationship with air temperature (Coughlan and Running 1997) that has been scaled by wind speed due to the fractional forest cover over a snowpack (Dunne and Leopold 1979). Advection melt is caused by

incoming precipitation and also rises in snowpack temperature considering heat capacity and density of water. More details about the equations used for snowmelt and accumulation processes within RHESSys model can be found at Tague et al., 2004.

2.2.5. Climate change scenarios

One of the objectives of this study is to investigate how climate change might change snowmelt timing, (and thus streamflow and DOC flux) in the future.

Hydrological models predict the possible response of hydrological parameters to changes in the various input conditions. Process-based hydrological models can simulate runoff, evapotranspiration, and changes in storage (including snowpack) in modeled watersheds through the use of empirical equations and physical processes.

Warmer winters will likely produce earlier runoff with lower snow water equivalent amounts, due to both reduced snowfall and earlier snowmelt. Table 2.2, shows the projected climate changes due to temperature changes expected for the Northeastern US. Table 2.3, presents the projected changes for precipitation changes for all four seasons.

Table2.2- Projected temperature changes in the Northeast US for the Mid- and End-of-century under Low and High emission scenarios

Northeast temperature		Mid-century (F)		End of century (F)	
		Low	High	Low	High
Winter	Mean	4.0	5.4	5.9	9.3
	Very likely	1.8	7.9	3.5	12.8
Spring	Mean	3.5	4.1	5.0	8.1
	Very likely	0.9	6.8	2.3	11.9
Summer	Mean	3.7	4.8	5.2	9.4
	Very likely	1.8	6.9	2.7	14.1
Fall	Mean	3.9	4.8	5.3	9.1
	Very likely	1.8	6.5	2.5	12.8

Data from USGCRP 2009

Table2.3- Projected precipitation changes in the Northern US for the Mid- and End-of-century under Low and High emission scenarios

Northeast precipitation		Mid-century (%)		End of century (%)	
		Low	High	Low	High
Winter	Mean	8	11	11	17
	Very likely	-4	26	-4	36
Spring	Mean	5	6	9	11
	Very likely	-5	17	-9	31
Summer	Mean	1	2	1	2
	Very likely	-12	14	-24	23
Fall	Mean	3	3	3	4
	Very likely	-9	16	-15	23

Data from USGCRP 2009

The table above, presents the climate change information for the Northeastern US, in terms of time periods, and in terms of climate variables (Temperature and Precipitation). Two time frames were chosen in this study; *mid-century* (2040-2070), and *end-of century* (2070-2100). There were 19 and 15 models run for the B1 (low emission) and A1 (high emission) scenarios respectively.

The *mean* range is the average of all the simulations. For the most *likely* range, the standard deviations above and below the mean for each scenario were computed. Then the minimum and maximum of those four values were reported as the *likely* range. The *very likely* range calculation was also determined to be the *likely* range with two standard deviations instead of one.

Within the next several decades, the Northeastern US is projected to experience an increase in annual mean temperature with the greatest increase occurring in the winter temperatures. This region is predicted to experience an increase in temperature of 3.8 to 9.0°F for the *mean* scenario and a *very likely* range of 1.9 to 12.5°F (USGCRP 2009) under the low and high emission scenarios. Furthermore, the Northeastern US is expected to experience an increase in winter precipitation with an average range of 8-17% under the low and high emission scenarios (USGCRP 2009).

For climate change scenarios, seasonal precipitation percent changes, and seasonal temperature changes for the Northeast region over the mid-century (2042-2051) and end-of-century (2082-2091) (as compared to the period 1963-1972) have been studied. The values have been predicted for emission scenarios ranging from the low (B1) to the high (A2). In this study, the *mean* and the *very likely* projections for both temperature and precipitation under the low and high emission scenarios for mid-century and end-of-century have been chosen. Eight scenarios

were run by RHESSys model to explore the impact of climate projections (both temperature and precipitation) on snowmelt timing.

Studying the impacts of both temperature and precipitation simultaneously, on changes in streamflow and snowmelt timing, may obscure the hydrological effect of the climatic variables when considered in isolation. So in addition to the previous analyses, we also ran the model by changing the climatic variables of temperature and precipitation one at time (i.e. changing seasonal temperatures according to the values in Tables 2-1 and 2-2 but maintaining current precipitation values, and vice versa). Therefore, another 16 scenarios were run to investigate the role of temperature changes and precipitation changes on snowmelt timing.

2.2.6. Streamflow center timing

Given the substantial changes in runoff that have occurred during the last 50 years, and the projected warming trends and precipitation changes, it is important that we investigate potential future shifts in streamflow timing.

To illustrate temporal trends in winter-spring streamflow, we measured the streamflow center timing at selected streamflow-gaging stations which have already reflected changes in the timing of spring snowmelt. Trends are based on the center timing of winter-spring streamflow which is the date when half of the total January 1–May 31 streamflow has passed by each streamflow gauge station. Monthly streamflow data were downloaded from the U.S. Geological Survey (USGS) (<http://www.usgs.gov/water/>) and the winter/spring center center timing was computed from (Stewart et al., 2005):

$$CT = \frac{\sum_{i=1}^{12} (t_i \cdot q_i)}{\sum_{i=1}^{12} q_i} \quad ; i = 1-12 \quad (\text{Equation 2.7})$$

Where CT is center timing, t_i is the time in months from the beginning of the water year (1 October) and q_i is the corresponding streamflow for month i . Therefore, CT is the value in months or days which show approximate time of the middle of the snowmelt period. In this study, the seasonal winter-spring (January 1 through May 31) center of -flow dates were computed.

This study also projected the streamflow-timing changes in terms of the CT in response to simulated climate changes during remaining portion of the 21st century. As described, the projected temperature and precipitation changes (Table 2.2 and 2.3) have been used as input to the RHESys model to study current temporal trends and to estimate changes in the center timing of streamflow in the future.

While several local climatic influences may also contribute to the most likely explanation for the changes in trends toward earlier snowmelt that have been recorded, here warmer winter and spring temperatures are considered in terms of a Temperature Index (TI). The TI is an average temperature over a gage that is specific for four months interval including: the average month of CT for a given gage (computed from equation 2.7), the two months prior, and the month after the average CT. The Temperature Index is specific for each gage and shows the air temperature variation during the critical seasons of snowmelt runoff (Steward et al., 2004).

Temperature Index (TI)

$$TI = \left(\sum_{i=1}^4 T \right) / 4 \quad (\text{Equation 2.8})$$

In addition to changes in winter/spring temperature, changes in precipitation, and more importantly precipitation form, can also impact snowmelt timing. Therefore, the impact of precipitation on streamflow center timing and on snowmelt timing is also studied here. Precipitation influences on flow timing are characterized by a Precipitation Index (PI), defined as the October-May average monthly precipitation.

$$PI = (\sum_{i=1}^8 P) / 8; \text{ Where: } 1=\text{Oct}, 8=\text{May} \quad (\text{Equation 2.9})$$

The relationship between historical CT anomalies and the TI and PI anomalies are estimated by fitting both linear and multiple regressions. These separate measures are introduced to quantify the effects of temperature only (linear regression), precipitation only (linear regression), and the combined effects of temperature and precipitation on streamflow timing (multiple regression).

2.3. Results

2.3.1. Precipitation partitioning methodology results

As described in methodology section, two approaches for precipitation partitioning were tested in this study. Figure 2.1, shows the Penobscot Watershed's simulated streamflow versus the observed streamflow using the RHESSys methodology to partition precipitation into rain and/or snow ($r^2:0.76$). Figure 2.2 and table 2.4, present the correlation between annual, monthly and daily RHESSys simulated streamflow versus Observed Streamflow.

The RHESSys model was run to simulate daily streamflow for the period of 2004 to 2012 for the Penobscot Watershed in state of Maine. The simulated results were then compared to

observed streamflow at the same gauge station (more information can be found at section 2.2.1 in this chapter describing model inputs). Generally, our RHESSys simulated results correlated well with observed streamflow at annual, monthly and daily steps (Figure 2.1 and Figure 2.2).

Despite the general good correlation between RHESSys simulated and observed streamflow, it should be noted that RHESSys simulated results tend to overestimate some peaks during the snowmelt periods, especially when the time of snowmelt coincided with heavy rainfall events (2005 and 2008). One of the reasons for this may be an uncertainty in the precipitation data inputs and the over-simplistic methodology used for partitioning the precipitation into rain/snow during the winter. It appears that the RHESSys's methodology for precipitation partitioning tends to over-estimate snowfall, and therefore over-estimate runoff when the snow starts to melt. Another factor that affects the streamflow simulation is the duration of precipitation events. Including an accurate measurement of the duration of each precipitation event could significantly improve the accuracy of simulated streamflow. However, such duration data are unavailable for our study area.

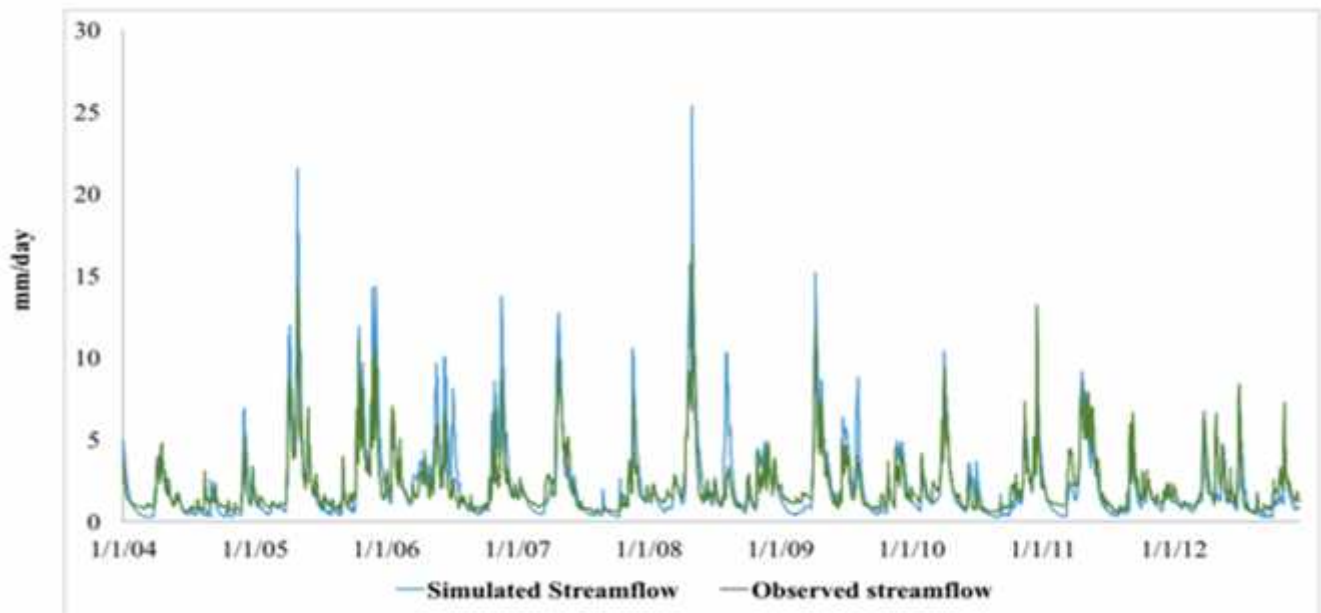


Figure 2.1, Penobscot watershed simulated (blue line) versus observed streamflow (green line) using RHESSys snow and rain partitioning methodology

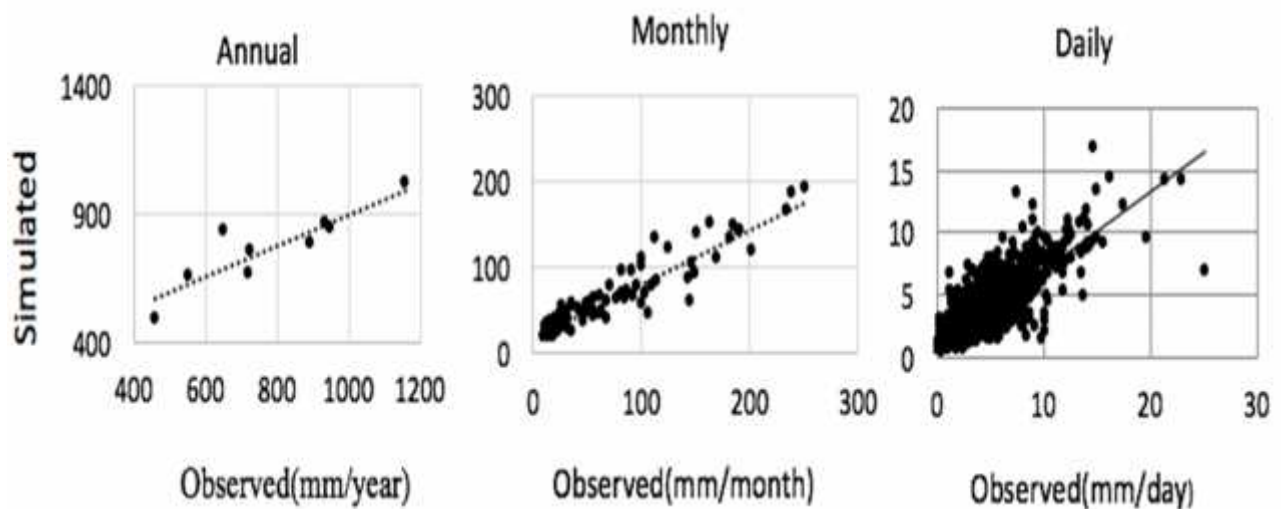


Figure 2.2, Annual, monthly and daily RHESSys simulated streamflow versus Observed Streamflow

Table 2.4, Correlation and Root mean square error between RHESSys simulated streamflow versus observed Streamflow

	Annual	Monthly	Daily
R	0.89	0.93	0.87
RMSE	103.1	27.9	1.27

As mentioned, another methodology (rather than the RHESSys original method) was also tested to see if that was better able to estimate snowfall and snowmelt related runoff. Figure 2.3, shows the daily simulated versus daily observed streamflow of the Penobscot Watershed using Dingman's methodology to partition precipitation into rain and/or snow ($r^2:0.71$) for the period of 2004 to 2012 at the Penobscot Watershed.

Our simulated result indicates that, even though the Dingman's method uses more climate variables to partition precipitation form, it appears to also overestimate snowfall, and therefore snowmelt runoff (2005 and 2008).

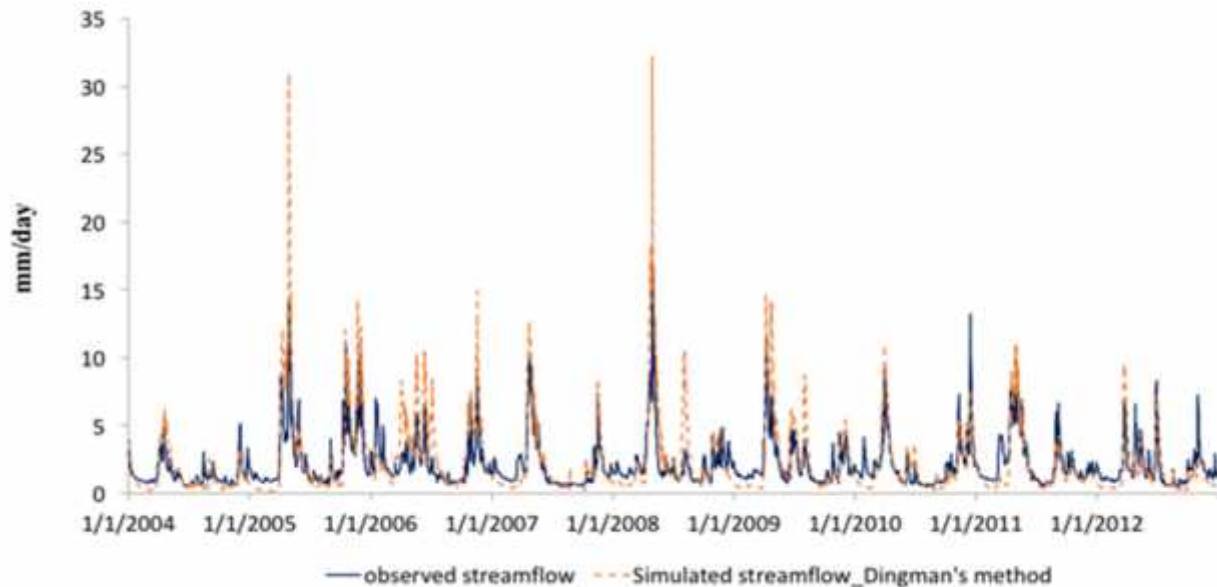


Figure 2.3, Penobscot watershed simulated (orange line) versus observed streamflow (blue line) using Dingman's methodology

Therefore, both the simulated results from the RHESSys inherent methodology (Figure 2.1) and the Dingman methodology (Figure 2.2), resulted in low flows during summer time which are somewhat less than the observed streamflow. However, the underestimation is less when using the RHESSys methodology and this would seem a preferable method despite the overestimation of high peak events.

2.3.2. Streamflow center timing results

As a way of looking at temporal trends in the winter/spring (January-May) streamflow, the center timing has been used as an indicator of changes in snowmelt melt timing. This methodology is easy and reliable, is comparatively insensitive to unrealistic inter-annual variations in flow, and represents a measure that is easily compared for basins in very different climatic regimes.

As mentioned, previous studies have shown significant trends toward earlier winter-spring streamflow in most stations in New England, especially in the northern and mountainous areas of Maine and New Hampshire, for the period of 1950-2000 (Dudley and Hodgkins, 2002). Therefore, we expanded our study into the timing of winter-spring runoff by evaluating the monthly streamflow time series from 1950 to 2011 at 27 USGS streamflow located across New England (Table2.5). Stations were selected from the Hydro-climatic Data Network (HCDN; Slack et al., 1988) and are considered to be free of substantial human influences (such as regulation, diversion, and land use-changes) and have long term periods of record.

Table2.5, USGS streamflow located across New England

USGS Station number	River name, State	USGS Station number	River name, State
1010000	St.John, ME	1064500	Saco,NH
1010500	St John2.ME	1073000	Oyster,NH
103500	Fish,ME	1076500	Pemigewasset,NH
1014000	St.John3.ME	1137500	Ammonoosue,NH
1022500	Narraguagus,ME	1078000	Smith,NH
1030500	Mattawamkeag,ME	1117500	Pawcatuck,RI
1031500	Piscataquis,ME	1118500	Pawcatuck2,RI
1038000	Sheepscot,ME	1121000	Mount Hope,CT
1047000	Carrabassett,ME	1188000	Burlington,CT
1052500	Diamond,ME	1204000	Pomperaug,CT
1055000	Swift,ME	1127500	Yantic,CT
1057000	Little Androscoggin,ME	1134500	Moose,VT
1060000	Royal,ME	1144000	White,VT
		1169000	North,MA

In this study, we evaluated the presence of trends in the winter/spring center timing, and for the local temperature (TI) and precipitation (PI) indices for the seasonal timeframe at the all 27 gauge stations across New England. Figure 2.4 and Figure 2.5, show the temporal trends in winter/spring streamflow center timing and temporal trends in regional temperature and precipitation index respectively for the period of 1950-2011. While, our analysis indicated significant trends toward earlier winter/spring streamflow (shown with red triangles ($P\text{-value} < 0.05$) and orange triangles ($P\text{-value} < 0.1$)) in the northern and mountainous areas of State of Maine, New Hampshire, Vermont and Massachusetts. For the stations shown with white triangles, statistically significant trends were not observed ($P\text{-value} > 0.1$). Furthermore, analyses of temperature (shown with orange circles) occur at most stations across New England, with some increases in the October through May precipitation at some stations in Maine, New Hampshire, Vermont and Connecticut (shown with blue circles). Purple circles for stations in Rhode Island and one station in New Hampshire indicated increases in both temperature and precipitation indices in those areas. The two stations located in Connecticut showed statistically insignificant change for both temperature and precipitation indices (gray circle).

Furthermore, the relationship between historical winter/spring streamflow center timing and the temperature index and the precipitation index are estimated by fitting both linear and multiple regression. Our results showed that changes in winter/spring streamflow center timing resulting in earlier dates were more related to increases in temperature rather than precipitation changes. The results are presented in table 2.6.

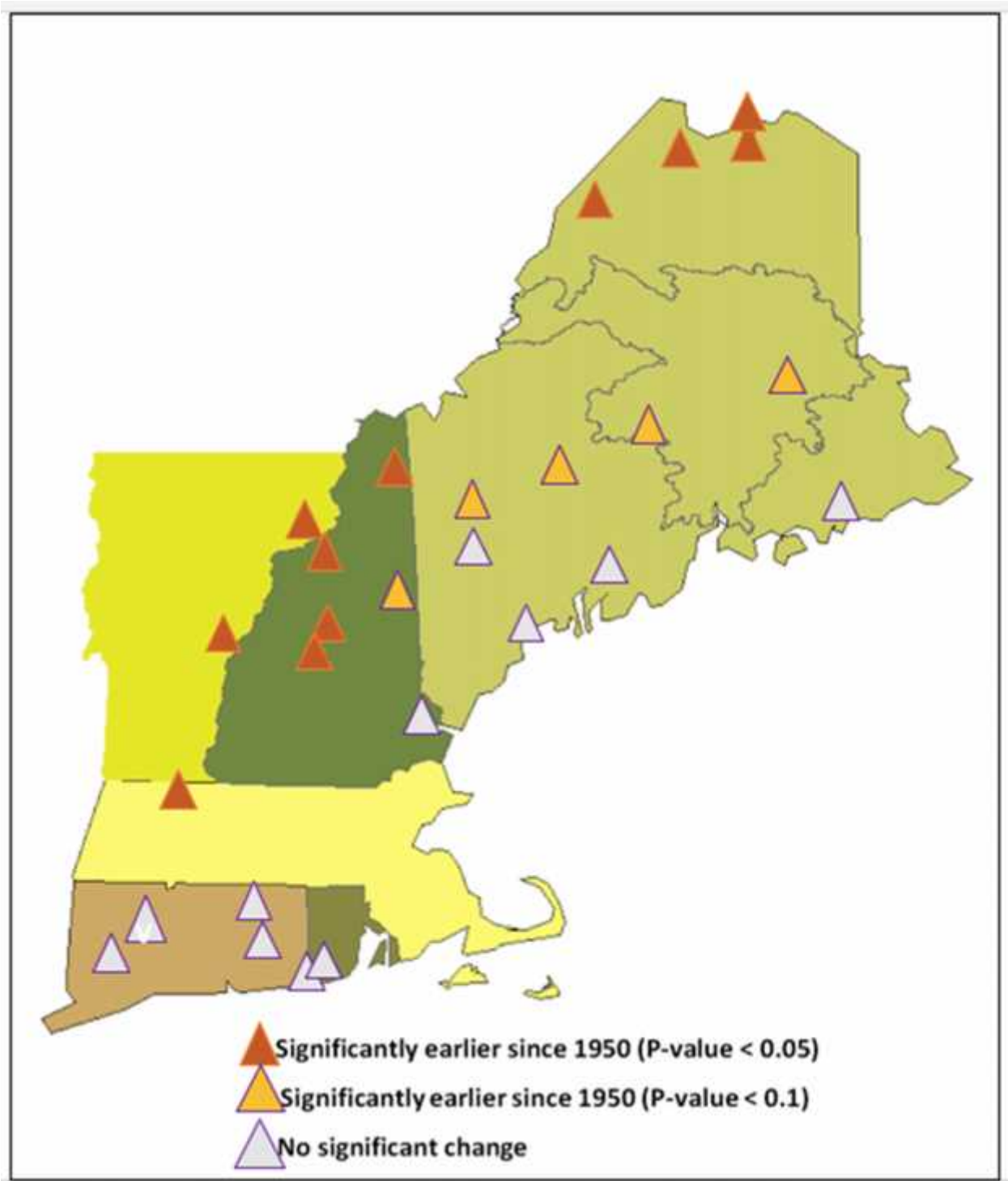


Figure 2.4, Temporal trends in snowmelt runoff across New England

Table 2.6, the relationship between historical winter/spring streamflow center timing and the temperature index and the precipitation index

USGS Station number	River name, State	CT, TI (r^2)	CT-PI (r^2)
1010000	St.John, ME	0.63	0.11
1010500	St John2.ME	0.53	0.13
103500	Fish,ME	0.47	0.16
1014000	St.John3.ME	0.71	0.18
1022500	Narraguagus,ME	0.25	0.32
1030500	Mattawamkeag,ME	0.18	0.25
1031500	Piscataquis,ME	0.65	0.18
1038000	Sheepscot,ME	0.18	0.21
1047000	Carrabassett,ME	0.48	0.23
1052500	Diamond,ME	0.45	0.17
1055000	Swift,ME	0.64	0.19
1057000	Little Androscoggin,ME	0.41	0.23
1060000	Royal,ME	0.53	0.26
1064500	Saco,NH	0.43	0.15
1073000	Oyster,NH	0.64	0.32
1076500	Pemigewasset,NH	0.63	0.17
1137500	Ammonoosue,NH	0.43	0.27
1078000	Smith,NH	0.57	0.21
1117500	Pawcatuck,RI	0.33	0.43
1118500	Pawcatuck2,RI	0.28	0.32
1121000	Mount Hope,CT	0.33	0.18
1188000	Burlington,CT	0.42	0.32
1204000	Pomperaug,CT	0.29	0.28
1127500	Yantic,CT	0.32	0.38
1134500	Moose,VT	0.36	0.57
1144000	White,VT	0.41	0.61
1169000	North,MA	0.53	0.32

It must be noted that changes in the amount and timing of seasonal flow as well as snowmelt related runoff would impact water resource and flood management systems in this region and would need to be considered by resource and policy managers. Therefore, we used the RHESSys model to evaluate the impact of future climate projection (presented in table 2.1 and 2.2) on winter/spring streamflow in the Penobscot Watershed. In order to evaluate the impact of climate change scenarios on winter/spring streamflow center timing shifts, we first looked at the simulated modeled results, using both the RHESSys and Dingman's methodologies of snow/rain partitioning, versus the observed winter/spring streamflows. Figure 2.6, shows the simulated versus observed winter/spring center timing for the period of 2004-2013. The simulated results are generated using both the RHESSys's and Dingman's precipitation partitioning methodologies. Table 2.7, shows the coefficient of determination (R^2) and Root mean square error between the simulated streamflows (RHESSys and Dingman) versus the observed streamflow. Both the RHESSys simulated results and the Dingman simulated results show good agreement with observed winter/spring streamflow center timing. The simulated streamflow results using the RHESSys methodology show that the temperature based methodology for the precipitation phase differentiation is better correlated with the observed streamflow than the Dingman's methodology. The results from RHESSys are slightly better due to better simulated snowfalls and therefore snowmelt related runoff in our study area, therefore we continued the rest of our study using only the RHESSys methodology for precipitation partitioning. However, it should be noted again that the uncertainty in the streamflow center timing does increase for future climate change scenarios reflecting the uncertainties in the modeling.

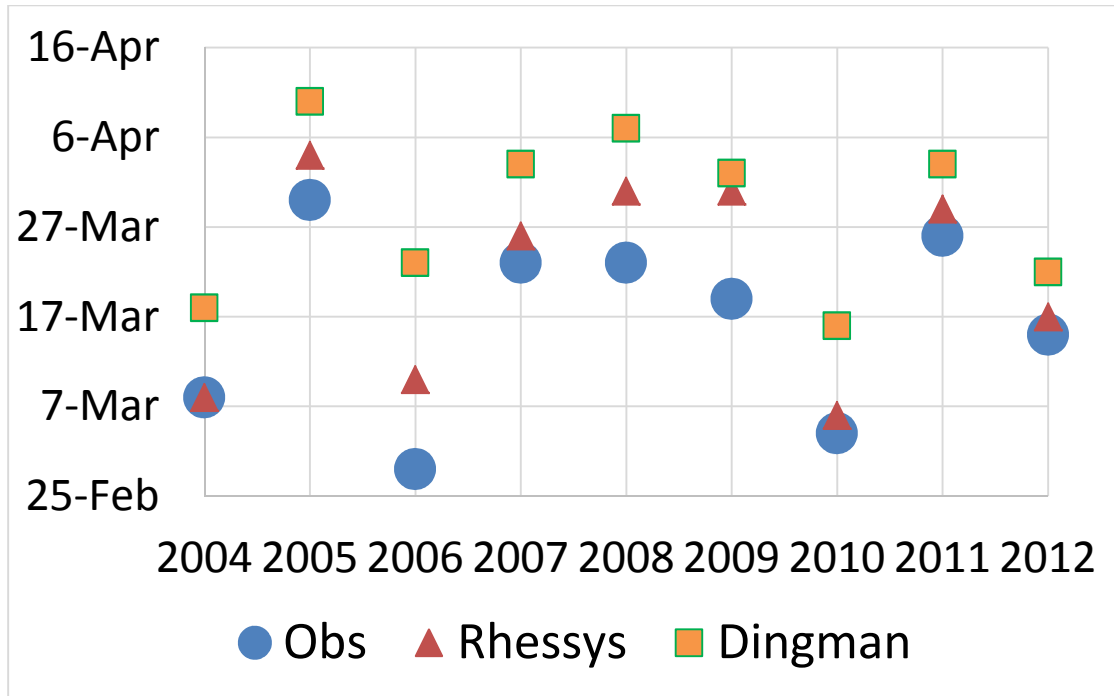


Figure 2.6, simulated (RHESSys and Dingman) versus observed winter/spring center timing

Table 2.7, Coefficient of determination (R^2) and Root mean square error between simulated streamflow (RHESSys and Dingman) versus Observed Streamflow

	RMSE	R^2
Obs-RHESSys	6.31	0.88
Obs-Dingman	13.11	0.81

We then, estimated the winter/spring streamflow center timing changes in terms of the CT expected in response to simulated climate changes during the 21st century. As described above, climate change projections are available for both *mid-century* (2040-2059) and *end-of-century* (2080-2099) under low and high emission scenarios considering the *mean*, and *very likely* projections. The *mid* and *end-of-century* projections are based on climate data from 1960-

1979 (although, unfortunately, the weather station located in the Penobscot Watershed has only acquired long term climate data since 1963). Thus, in order to be able to compare the changes in decadal intervals, we simulated the future scenarios for the periods of 2042-2051 and 2082-2091 and compared these with the observed climate data from the periods of 1950-1959, 1960-1969, 1970-1979, 1980-1989, 1990-1999 and 2000-2010. Table 2-8 and Figure 2.7, present the average decadal streamflow center timing results for both the previous years and the future years based on the future climate change scenarios (Mean and very likely scenarios under both low and high emissions) . Sample t-tests were used to evaluate the presence of trends in average decadal winter/spring streamflow center timing. Looking at the average decadal interval from 1950 to 2091 under the low and high emission projected scenarios as well as under a high emission scenario considering the *very likely* projections, (and using the RHESSys's methodology to partition precipitation), there appears to be a very significant trend toward earlier dates (P-value < 0.05). On the other hand, the average decadal interval from 1950 to 2091 under a *very likely* low emission scenario for both *mid* and *end-of-century* shows no statistically significant trends toward later dates (P-value > 0.1). This later timing corresponded to higher snowpack depth under this scenario due to a slight projected increase in temperature that still falls between the temperature threshold defined in RHESSys precipitation form partition method. Furthermore, projected decreases in precipitation under *very likely* under low emission scenario for both *mid* and *end-of-century* would also dampen the melt driven precipitation in the RHESSys snowmelt modeling. The shifts in winter/spring center timing towards earlier dates range from one week (Mean scenario under low emission) to three weeks (very likely under high emission) since 1950.

Table 2-8, Average decadal winter/spring streamflow center timing using RHESSys methodology

Year	Future scenarios			
	Mean-low emission	Mean-high emission	Very likely low emission	Very likely high emission
1950-1959	20-Mar	20-Mar	20-Mar	20-Mar
1960-1969	22-Mar	22-Mar	22-Mar	22-Mar
1970-1979	23-Mar	23-Mar	23-Mar	23-Mar
1980-1989	19-Mar	19-Mar	19-Mar	19-Mar
1990-1999	19-Mar	19-Mar	19-Mar	19-Mar
2000-2009	20-Mar	20-Mar	20-Mar	20-Mar
2042-2051	15-Mar	15-Mar	29-Mar	8-Mar
2082-2091	14-Mar	5-Mar	23-Mar	28-Feb
Results	Earlier dates P-value < 0.05	Earlier dates P-value < 0.05	Later dates P-value > 0.1	Earlier dates P-value < 0.05

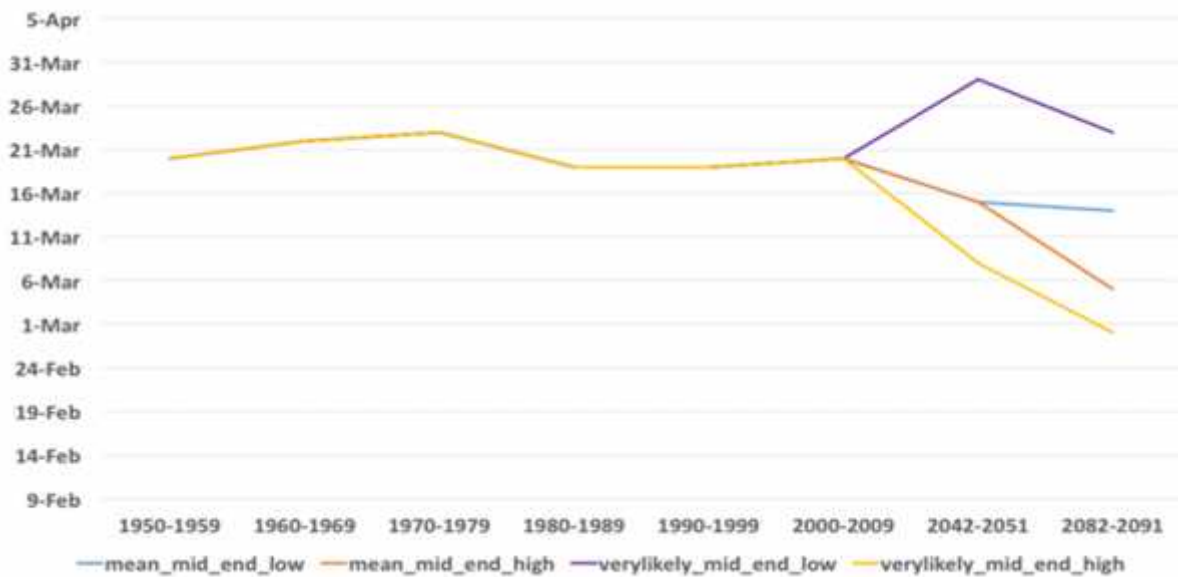


Figure 2.7, Average decadal winter/spring streamflow center timing

Precipitation has generally increased at high northern latitudes over the twentieth century with more precipitation falling as rain rather than snow (e.g. Mote, 2003; Knowles et al., 2006). A decrease of 20 - 30 percent in the amount of snowfall in State of Maine for the period of 1949-2015, is reported by the National Oceanic and Atmospheric Administration. In addition, another study (Kunkel et al., 2009) indicated a snowfall decrease of 0.6 – 0.9% per year for the period of 1930-2007 in the State of Maine. In figure 2.8, we explored the relation between the simulated rain to snow ratio (shown in percentage), January to May streamflow by changes in winter temperature for 1963-1971 (past and base time line) , current (2004-2013) and mid-century (2042-2051) and end-of-century (2082-2091) using RHESSys model. This figure illustrates how changes in average winter temperature along with changes in precipitation would impact rain/snow ratio as well as winter/spring streamflow. Our simulated results indicate that as winter temperature projected to increase in future, the ratio of rain to snow will increase in most scenarios, as well as increases in winter/spring streamflow. In *very likely* under low emission scenario for both *mid* and *end-of-century* the ratio of rain to snow is lower that resulted in higher snowpack and total volume of winter/spring streamflow is also less due to projected decrease in precipitation.

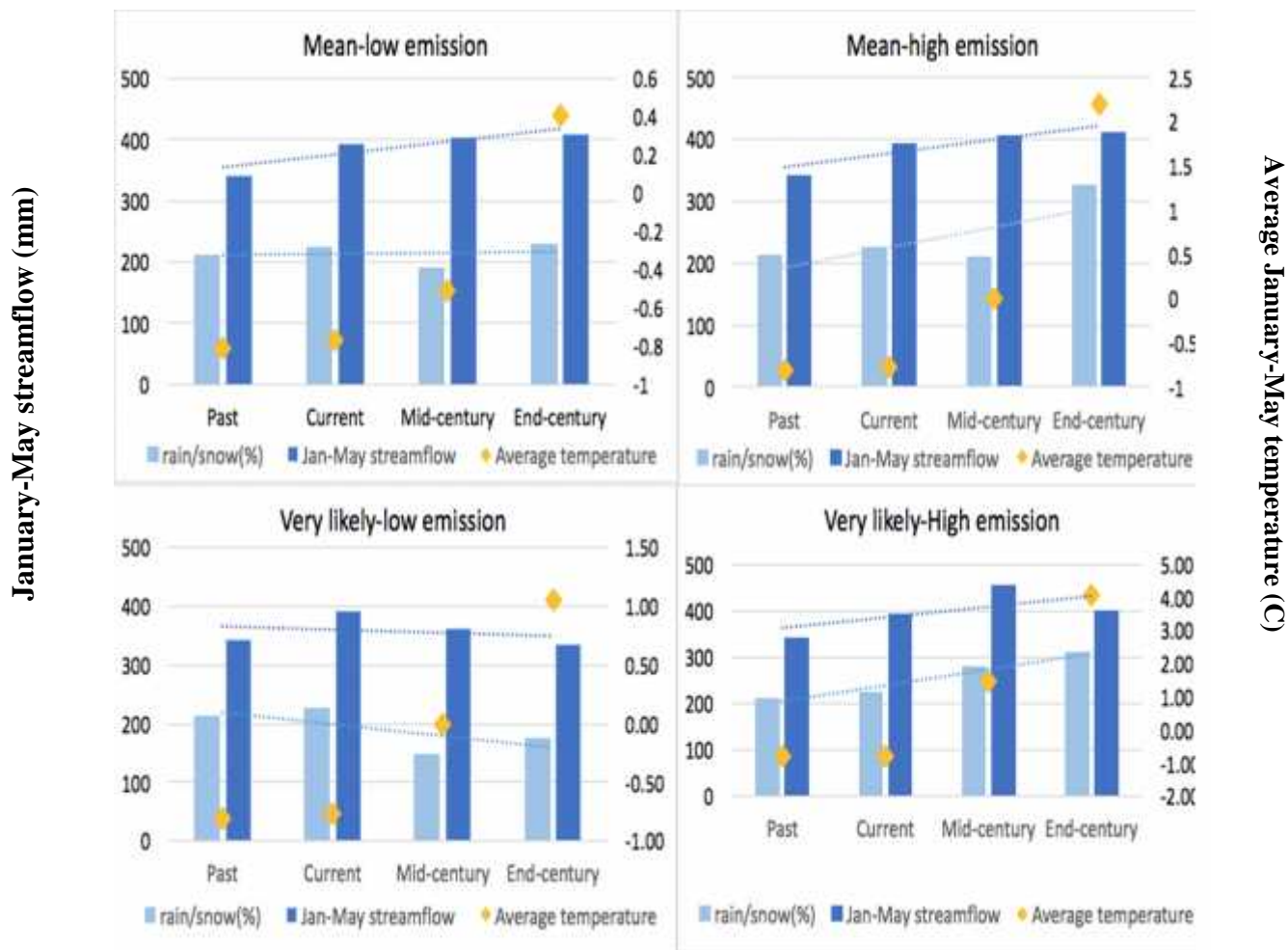


Figure 2.8, The proportion of rain to snow (%) and total winter/spring streamflow (mm) as compared to the average winter/spring temperature (°C).

2.3.3. Relation between streamflow center timing and climate variable changes

The effect of climatic forcing on streamflow has previously been observed with consideration of both temperature and precipitation simultaneously. However, simultaneous changes in both temperature and precipitation may obscure the hydrological effect of the climatic variables when considered in isolation. So, as described in the methodology section, in addition to the previous analysis, we ran the model by changing the climatic variables with only one or the other variable (i.e. changing seasonal temperatures according to the values in table 2-2 and 2.3 but maintaining the current precipitation values, and vice versa).

If the model is run by changing precipitation as predicted in the future scenarios and keeping the temperature as it is in the current situation, a significant change toward later winter/spring center timing will be observed in the period since 1950 for all climate change scenarios (P-value < 0.05). However, if the model is run using future temperature projections, but keeping precipitation as it occurs in the current situation, both the *mean* (significant, p-value < 0.1) and *very likely* (significant, p-value < 0.05) projections under the high emission scenarios show a trend toward earlier streamflow center timing since 1950. However, for the *mean* (although not a significant result, P-value > 0.1) and *very likely* (not significant, p-value > 0.1) projections under low emission scenarios, a trend towards later days is being predicted (Table 2.9).

Table 2-9, Average decadal streamflow center timing based on future climate projection

Future scenarios		Low emission	High emission
Precipitation only	Mean	Later days-P-value<0.05	Later days- P-value<0.05
	Very likely	Later days- P-value<0.05	Later days- P-value<0.05
Temperature only	Mean	later days- P-value>0.1	Earlier days- P-value<0.1
	Very likely	later days- P-value>0.1	Earlier days- P-value<0.05

2.4. Conclusions

Both the RHESys inherent methodology, (based on two temperature thresholds to differentiate rain and/or snow) and the Dingman et al., (2014) method (which considers station elevation, wet bulb temperature, and humidity) were applied to precipitation form partitioning in

the RHESSys model in order to investigate the uncertainties associated with the nature and inner structure of the model.

Our winter-spring simulated streamflow result corresponding to the RHESSys rain/snow partitioning method correlated well with observed winter-spring streamflow. However, an actual snowfall time series might decrease uncertainties in rain/snow partitioning and is something that should be considered in the future (although such measurements are hard to obtain).

In summary, future climate change projections show a trend toward earlier dates for the mean scenarios under both low and high emissions and also for the *very likely* scenario under the high emission projection. However, although future climate change projections for end-of-the-century under the *very likely* low emission scenario also shows changes in streamflow center timing towards earlier dates, for the mid-century under the mean low and *very likely* low scenarios, there is a trend toward later dates. This is most likely due to the predicted decrease in precipitation projected for mid-century under these low emission scenarios. Finally, by studying the relation between climate variable changes (temperature and precipitation) and the streamflow center timing, we can show that temporal changes in the streamflow center timing are most strongly connected to projected temperature changes.

All in all, considering the long term streamflow data, the Penobscot Watershed has already experienced changes in streamflow center timing toward earlier dates, indicating an earlier snowmelt runoff. Projections from climate models indicate that this trend will be continued into future resulting in more shifts toward earlier dates (mean scenario under both low and high emission and *very likely* scenario under high emission). The warmer regional winter temperatures appear to be the dominant force for the changes in streamflow center timing dates

in the Penobscot Watershed, and have a larger impact than the changes in the October through April precipitation amounts.

From a practical standpoint, it should be noted that there are several lakes and reservoirs located in the Penobscot Watershed and an earlier snowmelt runoff in this region could also threaten storage efficiencies. Furthermore, an advance in snowmelt runoff may also increase the length of summer droughts, with additional important consequences for ecosystem water supplies.

CHAPTER 3

SIMULATION OF DOC CONCENTRATION AND FLUX IN THE PENOBSCOT WATERSHED

3.1. Introduction

Dissolved Organic Carbon (DOC) is critical in linking terrestrial, estuarine, and marine carbon cycling (Richey et al., 2004) and DOC is one of the major forms of carbon in soil solution and in streams. Thus temporal changes in DOC in streams may indicate changes in the storage of terrestrial carbon (Bianchi et al., 2009; Williamson et al., 2008).

Although, DOC fluxes are small as compared to some other carbon fluxes in the ecosystem, they serve an important role in the carbon balances of litter and of the upper layer of soil (the O horizon) which make it possible to hydrologically transport carbon between different pools from forest floor into soil and into stream.

A number of watersheds have been experiencing increases in DOC transport as a result of increasing temperatures from climate change (Freeman et al. 2001). Some studies have suggested that this increase is also due to a reduction in the atmospheric deposition of sulfur (Evans et al., 2006). Several models, (the Mapped Atmosphere–Plant– Soil system – MAPSS (Gonzalez et al., 2010), and the dynamic model, MC1 (Bachelet et al., 2001), have been used to show that an increase in temperature will lead to an increase in vegetation density and carbon

sequestration across the United States, although conversely, very large increases in temperature may then cause shifts in vegetation types and that may result in changes in carbon storage as well as impact decomposition processes.

Thus an investigation of the temporal trends in DOC concentrations and flux as a result of changes in climate and land use will help us better understand the overall ecosystem carbon storage and fluxes.

Increasing DOC concentrations could also have important effects on the quality of drinking water (Haaland and Mulder 2009), on ecological processes, and on mercury dynamics (Forsius et al., 2010). Increases in terrestrially derived DOC concentrations in aquatic ecosystems may also lead to a rise in aquatic carbon dioxide emissions.

There have been several studies focused on identifying the relations between DOC concentration and potential ecosystem parameters. Aitkenhead and McDowell (2000), estimated the annual riverine DOC flux using soil carbon to nitrogen ratio (C:N) as a predictor; They found that the annual variance in fluvial DOC flux from various biomes can be predicted from the mean soil C:N ratio of that biome. Findlay et al., (2001), studied the relation between land use and its effect on both the quantity and character of DOC exported into rivers from surrounding terrestrial sources. Xenopoulos et al., (2003) analyzed the effect of nine catchment characteristics on DOC concentrations in lakes situated within North American temperate forests. They concluded that for temperate lakes, the proportions of lake perimeter and of wetland areas were the two most important controlling parameters for DOC predictions. Furthermore, they found that forested wetlands (especially with primarily coniferous vegetation) accounted for the largest proportion of lake DOC in their research area, and that scrub and shrub wetland and emergent vegetation did not play as important a role in the variability of lake DOC. The relation between

DOC concentrations and the abundance of wetlands and of water yield in the Penobscot Watershed has been investigated using the Spearman's rho correlation (Huntington and Aiken, 2013). Their results, and the results of other similar studies, indicate that the abundance of wetlands in a catchment could be shown to be positively related to streamwater DOC concentrations (Creed et al., 2008; Strohmeier et al., 2013; Huntington and Aiken, 2013).

In another study, Yang (2013), studied soil moisture and land-to-water carbon export in the urbanized Neponset Watershed by using remotely sensed data and the regional hydro-ecological model (RHESSys) and Tien et al., (2013), used a few landscape characteristics and the SWAT model to simulate daily runoff and to explain DOC concentration in the Neponset Watershed. They both explored the sensitivity of DOC flux due to rises in temperature. They predicted an increase in stream DOC will be tied to increases in temperature until the temperature reaches a threshold resulting in the limitation of vegetation growth.

Difficulty in obtaining frequent field measurements, along with a lack of consistency between laboratory studies and field measurements, have made it hard to obtain accurate estimations of the DOC in soil and the DOC flux from terrestrial to aquatic systems (Kalbitz et al., 2000). However, the Regional Hydro-Ecological Simulation System (RHESSys) gives us an opportunity to explore and simulate the details of the Penobscot Watershed biogeochemistry. RHESSys integrates several existing independent models. For instance, RHESSys incorporates a modified BIOME-BGC Model (Running et al., 1993) to account for carbon and water cycling. Many of the sub-models within RHESSys have been altered and extended to improve the simulation of biogeochemical processes in both the soil and canopies. Soil organic matter decomposition in RHESSys follows the CENTURY Model (Parten et al., 1996).

3.2. Data

In this research, the RHESSys model has been used to simulate the DOC patterns in the Penobscot Watershed. Remotely sensed data were used in this study to provide the spatial input data required by RHESSys to create flowpath and landscape representations. In addition, field measured DOC concentration data, USGS gauge station stream flow data, and climate data (maximum and minimum temperature and precipitation) were also used in this study to calibrate and validate the simulated DOC concentrations and fluxes. More information about the streamflow and climate data that were used in this study described in chapter two (Section 2.2).

The field measured DOC concentration and flux from the Penobscot Watershed used in this study for validation were obtained from continuous discharge measurements and the discrete water sampling done by Huntington and Aiken (2013). Our simulated DOC flux and concentrations were then compared with observed measurements, and also with results from the LOADEST regression model (Huntington and Aiken, 2013).

3.3. The carbon cycle simulation in RHESSys

As discussed, RHESSys is a semi-mechanistic carbon cycling model in which carbon is balanced. Carbon, nitrogen in the plant, litter and soil components is defined in the model. During carbon cycling in RHESSys, carbon will be fixed by plants from atmospheric CO₂ as a function of temperature, nutrients, radiation, and water availability. The amount of carbon left after vegetation respiration is then allocated to the various parts of plants (First carbon Pool; leaves, stemwood, fine roots). There are four litter and soil pools defined in RHESSys (Secondary carbon pools). The DOC in soil solutions is produced from the decomposition processes in the secondary carbon pools (soil and litter carbon pools). The decomposition rate is

estimated by first using base decomposition rates for the different litter and soil pools, and then is scaled by soil temperature, nutrient availability and soil water content. Nutrient availability impacts both photosynthesis and decomposition processes within RHESSys modeling. A partitioning strategy followed by Landsberg and Waring (1997) is used in RHESSys model to simulate the impact of nutrient availability and soil moisture content on species specific allocation ratios. Soil biogeochemistry and nutrient cycling are modeled at a patch level within the watershed. More information about spatial levels within the RHESSys model has been described in chapter one.

RHESSys simulates the vertical and lateral soil moisture for each patch object and the DOC flux is associated with these flows at the patch level (a Patch is the smallest spatial scale in RHESSys, created from combining the DEM, the soil map, the vegetation map and the land cover map, (more details can be found in chapter one)).

The precipitation that reaches the soil surface after being intercepted by the vegetation will be infiltrated into the soil layers (Philip's infiltration equation, 1957) and some part of it will become surface flow and will be discharged to the adjacent lower elevation patches. A three-layer model (root zone, unsaturated zone, and saturated zone) is defined in RHESSys to simulate the vertical fluxes for that part of the throughfall that infiltrates into the soil. Finally, when the soil layers are saturated, the lateral flow carries the DOC out from the soil. The amount of DOC that gets leached out from the soil is a function of soil porosity, the decay rate of soil porosity, the soil depth at defined layers (root zone, unsaturated and saturated zones), the available DOC in the soil, the DOC distribution with depth, the DOM production rate, the DOC absorption rate and the soil water content. Figure 3.1, shows a simplified carbon cycle and the DOC production and transportation processes in RHESSys.

Soil physical characteristics along with vegetation physiological traits representing the study area are all defined in soil and vegetation default files as an input in RHESSys model (initialized by field measurements and/or previous studies). Since RHESSys is a semi-mechanistic carbon cycling model, it uses a set of mathematical representations of the key processes controlling the carbon cycling dynamics within an ecosystem. Carbon cycling estimation within RHESSys model includes the estimation of photosynthesis (Farquhar photosynthesis model, Farquhar et al., 1980), vegetation respiration (Ryan model, Ryan 1991), vegetation allocation processes and turnover rates (as vegetation specific parameters and scaled by environmental factors) and soil decomposition and respiration rates. More details about the mathematical equations used in each sub-model of RHESSys can found in Tague et al., 2004.

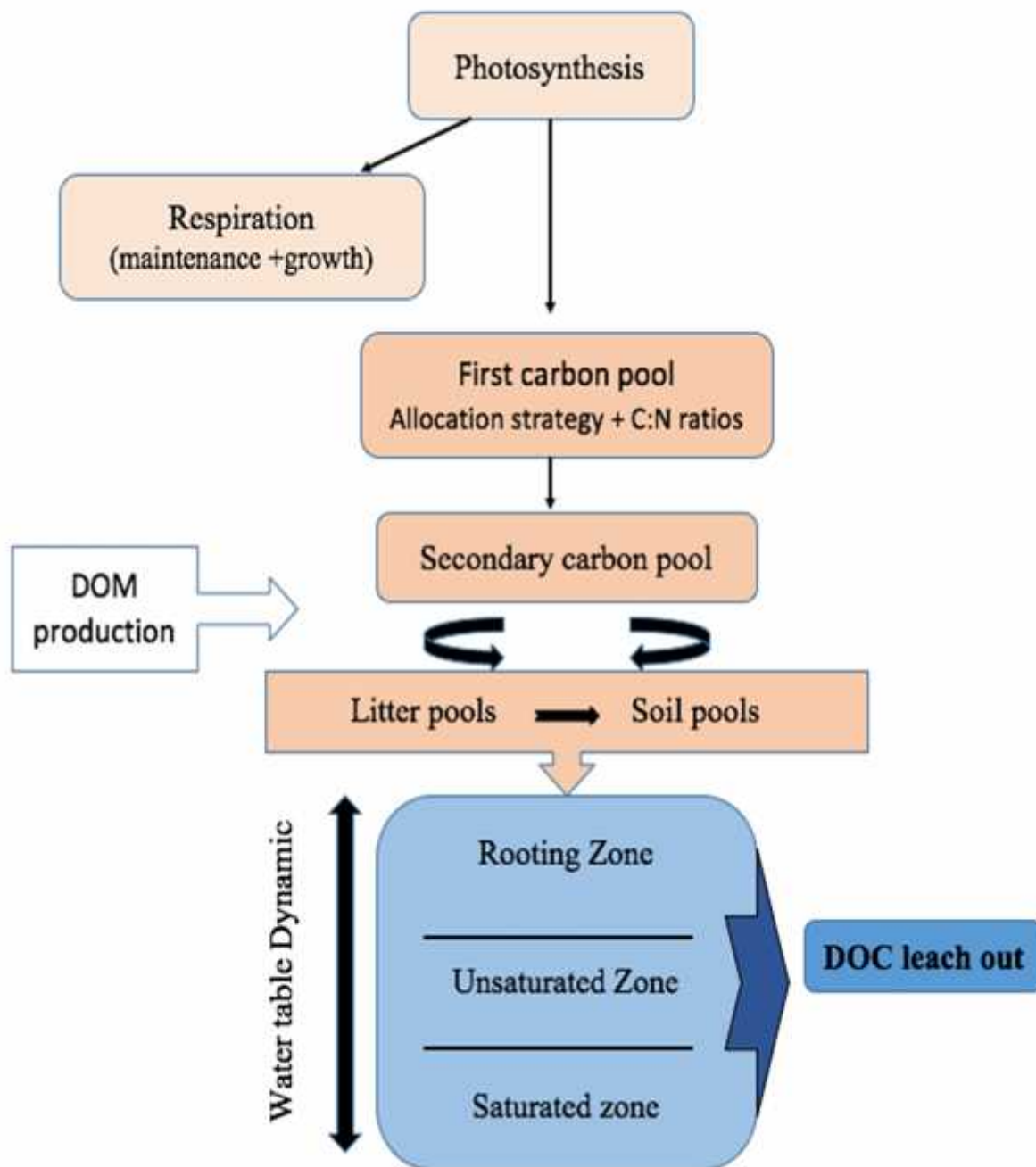


Figure 3.1. Simplified carbon cycle and DOC production and transportation processes in RHESSys

3.4. Sensitivity analysis

Physical hydro-ecological models enable us to better understand how various parameters impact a simulated result (in this case we are focused on streamflow DOC simulations).

In a study on soil moisture and land-to-water carbon export in the urbanized Neponset Watershed, Yang (2013) explored the sensitivity of the streamflow DOC as simulated by RHESSys model to various parameters. In her research, sensitivity analyses were performed for groups of parameters: DOM_decay_rate, DOC_production_rate, temperature, nitrogen deposition rates, soil depth, the ratio of infiltrated water that bypasses soil directly into a deeper groundwater table, and the C: N ratio of leaf litter.

Yang (2013) found that slightly higher DOM_production_rates, nitrogen deposition amounts, and temperatures, as well as a deeper soil depth, can lead to increased stream DOC flux and concentrations. Any increase in the stream DOC flux and concentration caused by increasing the nitrogen deposition only occurs until the nitrogen is no longer a limiting factor for vegetation growth. Also, it should be noted that the sensitivity of stream DOC changes to changes in nitrogen deposition, are also related to initialization of soil C:N ratios in the research area. The nitrogen required for microbial processes depends on the soil C:N ratio and nitrogen deposition.

Furthermore, the Yang (2013) study concluded that rises in temperature may also act as a limiting factor for vegetation growth after some optimum threshold. Further rises in temperature beyond this threshold will only increase the respiration rate and will therefore decrease stream DOC flux and concentration.

In-stream DOC is tightly linked to both the ecological processes and hydrological processes, but the physiological parameters defining these processes are difficult to measure and

there is a lot of uncertainty in these values. Because of the heterogeneity of the large Penobscot Watershed landscape (the largest watershed modeled thus far with the RHESSys model), we performed sensitivity analyses on some of these parameters, including the DOM_production_rate and the DOC_absorption_rate.

The DOM_production_rate in RHESSys is based on the soil parameter of each soil class with a range from 0-1 specific to each soil types. The DOM_production_rate influences both the ecological and hydrological aspects of the of DOC simulation. In this study, we explored the sensitivity of stream DOC flux to changes in DOM production rate. Figure 3.2, shows the average daily streamflow DOC flux under a changing DOM production rate. This sensitivity analysis reveals that the mean daily stream DOC flux increases with an increase in the DOM_production_rate until some threshold (30% increase), where it then levels off and begins to decrease when higher DOM_production_rate would result in nitrogen limitation for vegetation growth. The average daily stream DOC flux increases from 0.0324 to 0.0332 (g/m²/day) when the DOM_production_rate was set to increase from the optimum rate after the model parameterization to an increase of 30% of DOM_production_rate. Also, a 50% decrease in the rate of DOM_production_rate, resulted in a decline in the average daily stream DOC flux to 0.0319 (g/m²/day) from the optimum value (0.0324 (g/m²/day)).

The DOM production rate parameter, in the RHESSys model, is set to allow the conversion of a fraction of the litter carbon into DOC and DON (Dissolved Organic Nitrogen). Note that although a higher DOM_production_rate can mean more litter carbon is converted to DOC and DON, a very high DOM production rate can also cause an increase in the loss of nitrogen available for plants to uptake. In addition, higher DOM production rates mean more water consumption by plants during the decomposition processes. Those two factors will

eventually decrease the amount of potential DOC that can be leached out into the streams because they will slow the rate of carbon assimilation by the vegetation.

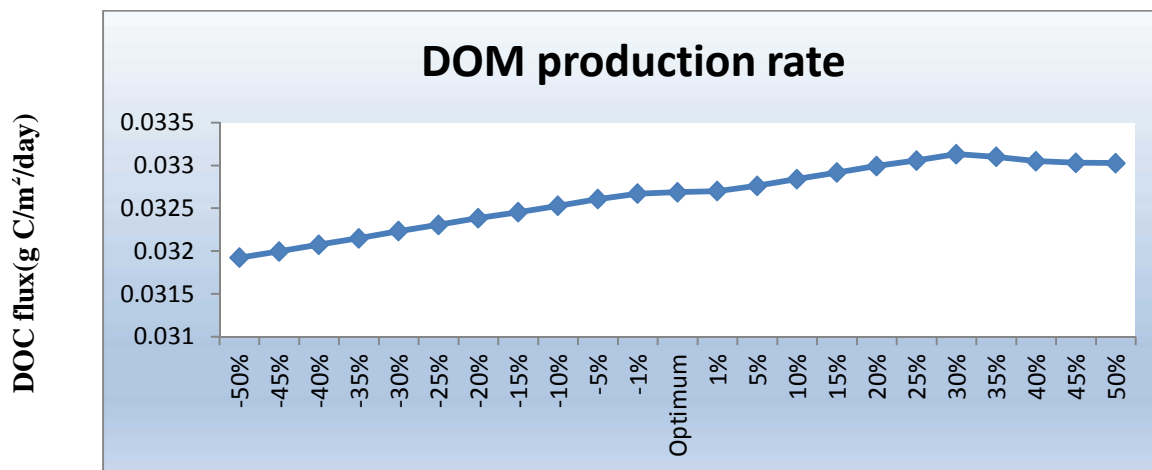


Figure 3.2. Stream DOC flux changes as a function of the DOM_production rate

The DOC_absorption_rate is another soil specific parameter that is used to estimate the amount of DOC that can potentially be absorbed in the soil. Some fraction of the absorbed DOC will be leached out during precipitation events that are sufficiently large to generate lateral transport. The higher the DOC_absorption_rate, the less DOC is leached out of the soil for a given precipitation event. Figure 3.3, illustrates the streamflow DOC flux changes with respect to changing DOC absorption rates. The results indicate that even a decrease of 10% DOC absorption rate from the optimum value can lead to a large increase in the amount of streamflow DOC that is leached out of the watershed. In the Penobscot catchment, the existences of large reservoirs appear to greatly affect the DOC absorption rates and the streamflow DOC fluxes.

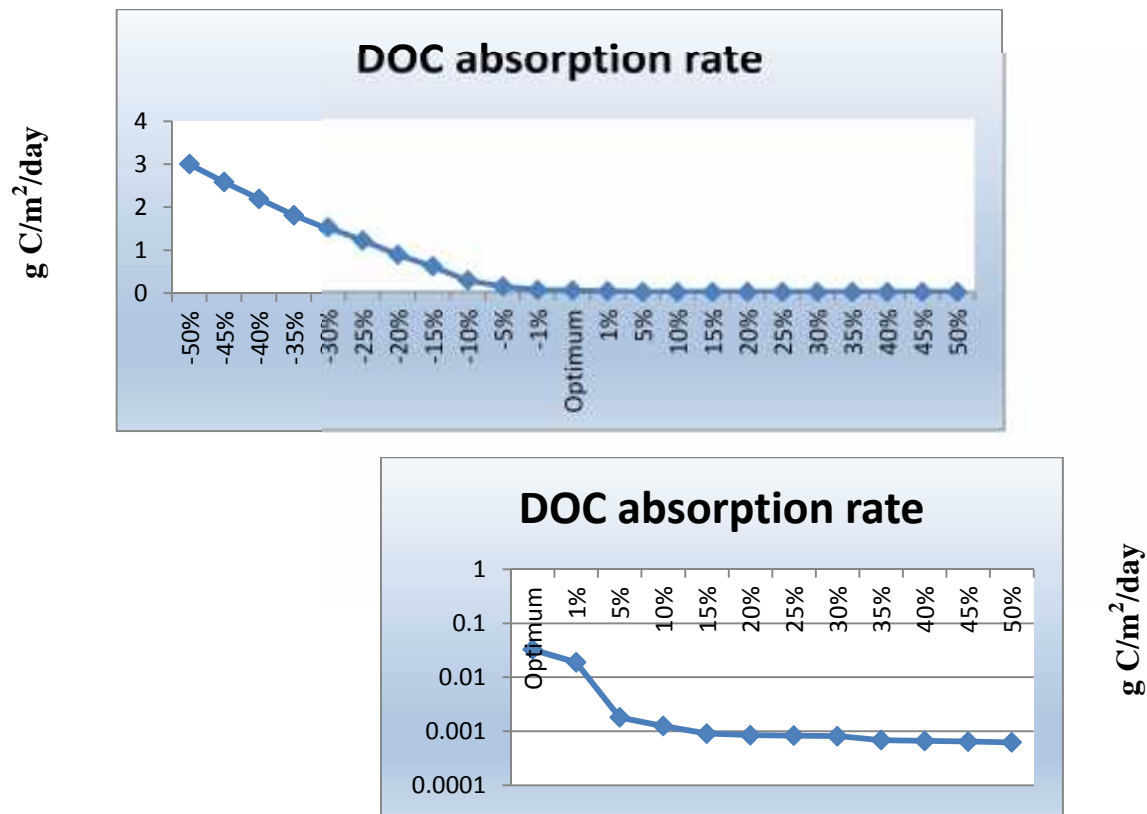


Figure3.3, Stream DOC flux changes as a function of the DOC_absorption_rate

3.5. Results

3.5.1. Simulated Daily stream DOC Concentrations and Flux

The daily Penobscot Watershed DOC flux and concentration are compared with observed values for the period of 2004-2012. Figure 3.4, shows the simulated DOC flux (Orange line) and observed values (purple points) at the bottom and simulated streamflow (back line) and observed streamflow (green line) at the top. The simulated DOC flux correlates well with the observed values ($r: 0.66$). The correlation is highest during winter time (0.86) and lowest in spring (0.6). Among the simulated years (2004-2013), the year 2004 had the lowest streamflow DOC flux, which also corresponded to the lowest streamflow and precipitation amounts for that year. The

high peak of DOC flux in 2005 occurred during the time of snowmelt and may be caused by the accumulation of soil carbon during the previous year (2004). This high peak also coincided with higher precipitation amounts in 2005. During 2005; heavy precipitation events carried a large amount of DOC in to the streams. It must be noted that in 2006, there were lower amounts of DOC in the streams, even though the precipitation amounts and the streamflow for 2006 were almost as large as those for 2005. However, there does not appear to have been sufficient stored DOC in the soil from 2005 to lead to high DOC amounts in the soil solution for 2006. This tendency towards a memory has also been noted in other studies, indicating that the stored DOC concentration in one year can impact the DOC export in the following year (Yurova et al., 2008). Huntington and Aiken (2013), also noted that the unusually high precipitation in 2005 depleted (flushed out) the soil DOC so that the comparably high precipitation and runoff in 2006 did not result in similarly high DOC export. This short term change in the concentration discharge relation indicated that, in this case, the DOC was supply limited.

The correlation between the streamflow DOC flux and the observed DOC flux are higher during the winter and spring times (r : 0.72) and somewhat lower during summer and autumn (r : 0.55). The model overestimated the DOC flux during the periods where the snowmelt coincided with extreme precipitation events in 2005 and 2009 and again during the high precipitation events in the late fall of 2005. Figure 3.5 illustrates the logarithm scale of the simulated daily streamflow DOC flux (green line) as compared with the observed DOC flux (red points) to better investigate the low values (correlation: 0.79).

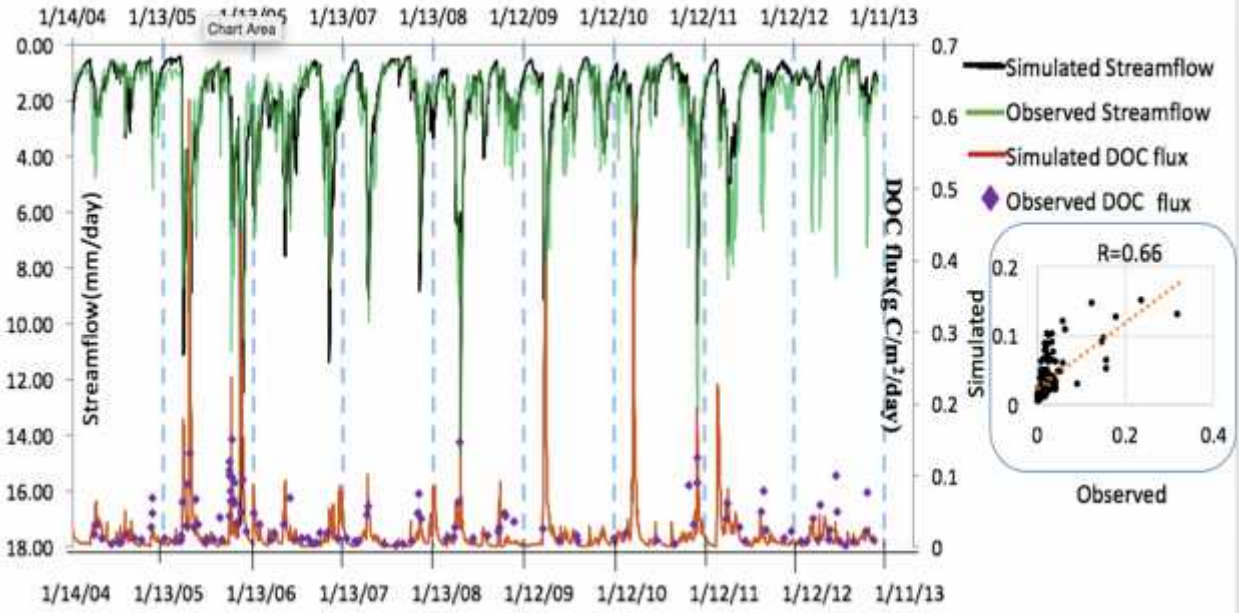


Figure 3.4, simulated daily DOC flux compared with observed DOC flux (at the bottom, g C/m²/day) and simulated daily streamflow and observed daily streamflow at the top (mm/day)

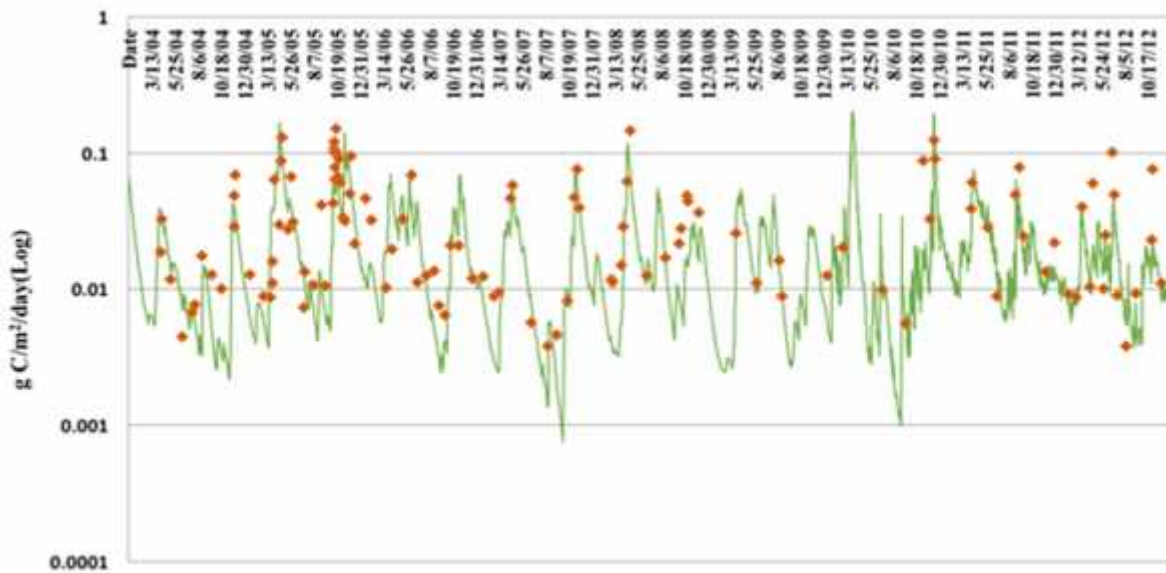


Figure 3.5. Simulated daily DOC flux compared with the observed DOC flux

We then compared the simulated DOC concentration with observed DOC concentration values in the Penobscot Watershed for the period of 2004-2012 and also looked at the average monthly DOC concentration for the period of 2004 to 2012. Figure 3.6, shows the simulated daily streamflow DOC concentration (Orange line) with the observed DOC concentrations (purple points) and the simulated daily streamflow (back line) with the observed streamflow at the top (green line). The correlation between the simulated DOC concentrations and observed values ($r = 0.42$) are lower than for the DOC flux. The simulated DOC concentrations were calculated from the simulated DOC flux and the simulated streamflow data, so uncertainty in any of those simulated results impacts the simulated DOC concentrations. In addition, generally, the simulated monthly average DOC concentrations were highest in July followed by August and were lowest in March in the Penobscot Watershed.

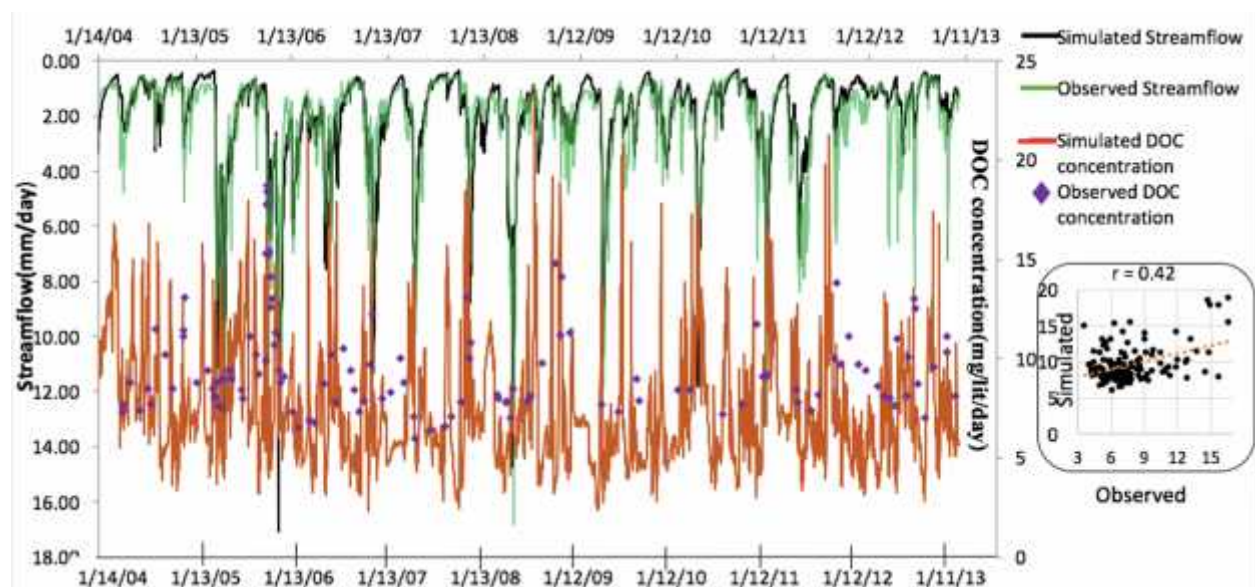


Figure 3.6, Simulated daily DOC concentration compared with observed DOC concentration (at the bottom, mg C/lit) and simulated daily streamflow and observed daily streamflow at the top (mm/day)

In order to further compare the simulated streamflow DOC flux with the measured values, we also compared the RHESSys simulated results with the modeled values from the empirical LOADEST model (Huntington and Aiken, 2013). Although the empirical LOADEST model does not allow investigation of impact of the myriad of inputs used in RHESSys, it has been successfully used to capture the overall flux and concentrations amounts associated with the Penobscot Watershed. We also focused on some of the sub-watersheds inside the larger Penobscot Watershed and compared these RHESSys results with the LOADEST simulation results for these sub-watersheds as well. The locations of these sub-watersheds within the Penobscot Watershed are shown in the figure 3.7. The Load Estimator (LOADEST) regression program was used to estimate the DOC export by using daily river discharge data, plus paired, discrete instantaneous discharge data, and DOC concentration data (Runkel *et al.*, 2004). LOADEST predicts the variation in DOC concentration as a function of time of year and rate of discharge. Table 3.1, shows the RHESSys streamflow DOC simulations as compared with the LOADEST simulation results from the Penobscot Watershed and three of the sub-watersheds inside the larger Penobscot Watershed. The RHESSys simulated results compare well with the LOADEST from the large Penobscot Watershed and sub-watersheds.

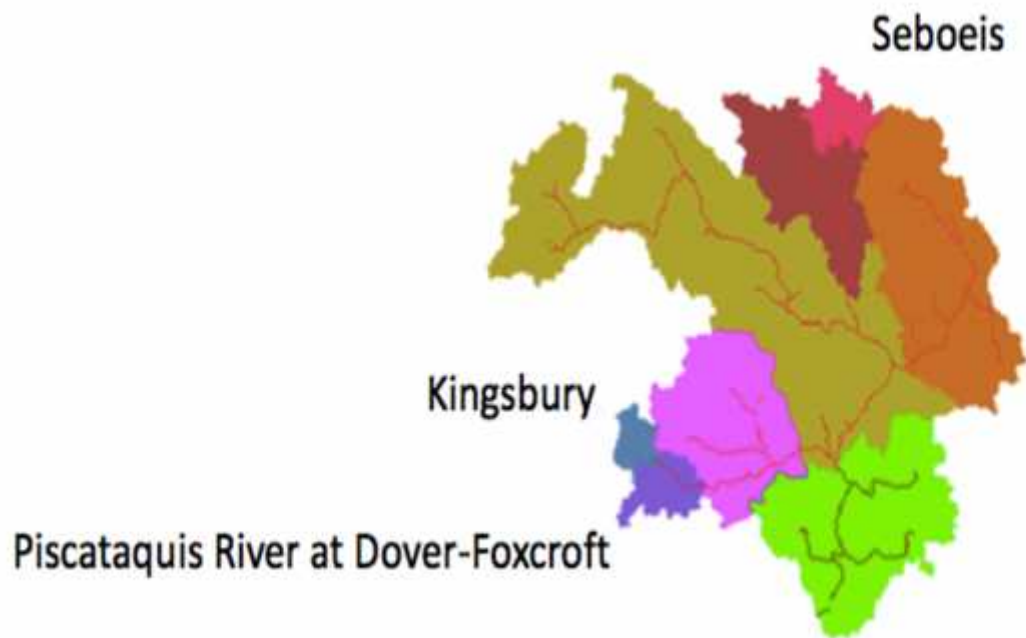


Figure 3.7, sub-watersheds inside the larger Penobscot Watershed

Table 3.1, RHESSys and LOADEST streamflow DOC comparison

Gauge station	Model	Average DOC flux (Mt C/d) (2004-2007)	DOC yield (Kg C/ha/year) (2004-2007)
Penobscot at Eddington	RHESSys	407	74
	LOADEST	392	71
Subwatersheds in the Penobscot Watershed		Cumulative DOC flux (Mt C) (2004-2005)	DOC yield (Kg C/ha/year) (2004-2005)
Kingsbury stream near Abbot Village	RHESSys	4.22	63
	LOADEST	4.74	70
Seboeis	RHESSys	7.05	51
	LOADEST	7.39	53
Piscataquis at Dover Foxcroft	RHESSys	12.67	63
	LOADEST	14.6	71

3.5.2. The impact of climate change scenarios on the DOC flux

As discussed, climate factors can play an important role in both the production and transport of DOC. Climatic drivers can include temperature (e.g. Freeman et al., 2001b; Evans et al., 2006), soil moisture impacts on the decomposition processes (e.g. Worrall et al., 2006), solar radiation (e.g. Hudson et al., 2003), and variation in the timing and intensity of precipitation and snowmelt (e.g. Hongve et al., 2004; Erlandsson et al., 2008).

There are several studies showing increases occurring in the current DOC flux as compared to the past. Increases in DOC and in proxies of DOC, such as water color, have been reported from many catchments in Europe and North America (Freeman et al., 2001a; Skjelkvåle et al., 2001; Löfgren et al., 2003; Hongve et al., 2004; Evans et al., 2005; Worrall et al., 2005; Vuorenmaa et al., 2006). Increases have also been reported from Swedish and Norwegian sites since the mid 1960s (Andersson et al., 1991; Löfgren et al., 2003; Hongve et al., 2004). Furthermore, predictions of the future annual DOC export from the Penobscot River, based on the LOADEST model, combined with climate projections for the northeastern US, as generated by the United Kingdom Meteorological Office, indicate the potential for a substantial increase in DOC export over the next 80 years (Huntington et al., 2016).

Climate factors can play an important role in both DOC production and hydrological processes influencing DOC fluxes. Changes in temperature would impact photosynthesis rate as well as respiration rate, evapotranspiration and decomposition processes. Also, changes in precipitation would impact soil moisture content regulation DOC flux and influencing water availability for vegetation growth and decomposition processes. The impacts of changes in climate variables are complex and we need to consider the combined impact of them on different

processes. Terrestrial export of DOC depends on net primary production, solubility and hydrological process influencing both DOC production and transport within the ecosystem.

The process based hydro-ecologic model (RHESSys), used in this research, allows us to explore how the various climate variables will impact future simulated DOC flux

Given the projected changes for the climate of Northeast America, as described in chapter 2, we focused on modeling the climate-induced changes in streamflow DOC flux under eight selected climate scenarios (*Mean and very likely* scenarios under *low and high emission* for both *mid* and *end of the century*). To understand the potential impact of climate change on streamflow DOC flux, we first validated our model with current measured DOC flux and concentration values (figures 3.4 and 3.6) and then simulated the dissolved organic carbon values for the future. We looked at the annual changes as well as the seasonal patterns. The relationship between the changes in each climate variable (temperature and precipitation separately) and the potential impact of changing both climate variables at the same time (as is projected for the future according to USGCRP,2009 for the Northeastern United States) were all investigated. Figure 3.8, shows the percentage changes of annual average streamflow DOC flux as compared to our base time line (1963-1972) for the combined impact of projected changes in the climate variables. It should be noted that, the current time period includes 2004-2012 and the projected future values for *mean* and *very likely* range under low and high emission scenarios are computed for both *mid* (2042-2051) and *end-of-century* (2082-2091). The percentage change in annual average DOC flux in each of these time periods is compared with our base time line (1963-1972). More information about projected temperature and precipitation changes under each scenario can be found in chapter two, Tables 2.1 and 2.2.

Our simulated results (Figure 3.8) indicate an increase of 32% in average annual DOC flux from the current time period (2004-2012) to base time line (1963-1972). An almost 9% increase in average annual DOC flux for the *mean* scenario under *low* emissions, a 14.5% increase for the *mean* scenario under *high* emissions and a 14% increase for the *very likely* scenario under *high* emissions are predicted from our simulated RHESSys results. Despite the projected increases in average annual DOC flux from most of the scenarios used in this study, a 5% decrease is also predicted for the *very likely* scenario under *low* emissions where a projected decrease in precipitation and a slight increase in temperature are reported for this scenario. Even though, the simulated results show an increase in the amount of streamflow DOC flux since the 1960s, the model predictions for the future are less than the current time period, which can be explained by the adverse impact of further rises in temperature on evapotranspiration, respiration, photosynthesis, and decomposition processes.

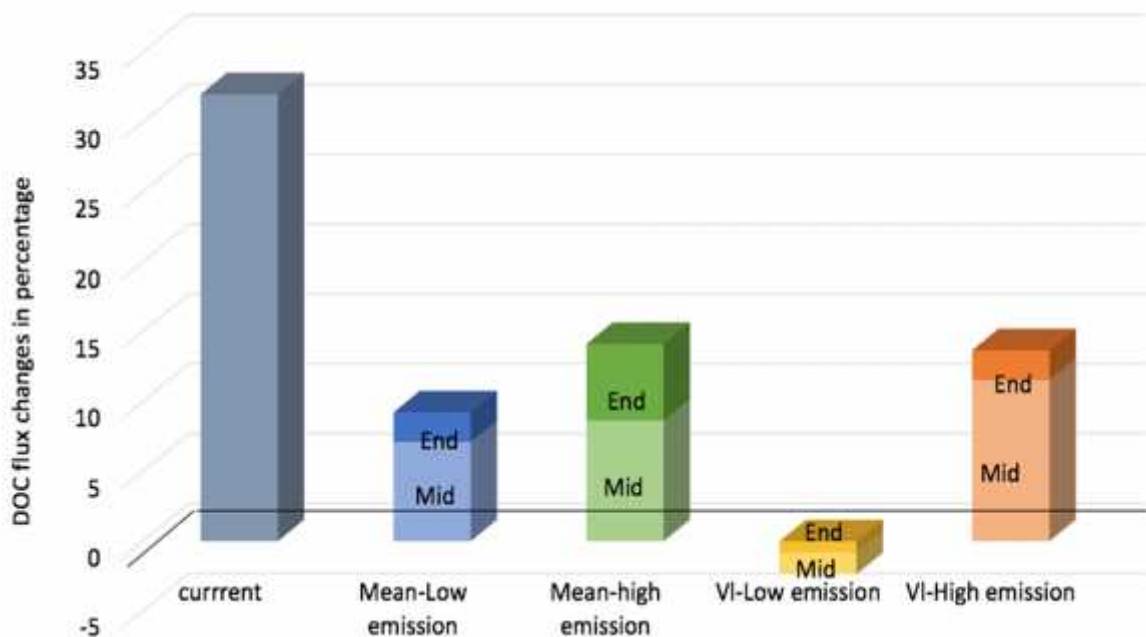


Figure 3.8, Average annual DOC flux changes in percentage

Our modeled results indicate that projected increases in temperature in future, will result in predicted increases in the evapotranspiration rate, while streamflow is simulated to be decline in future as compared to the current time line (2004-2012). DOC flux and streamflow are positively correlated, so any projected decrease in streamflow in the future would also result in a decrease in DOC export. In addition, the rate of evapotranspiration and DOC flux are negatively correlated. So, any projected increase in evapotranspiration would result in decreases in the DOC flux.

Furthermore, rises in temperature would enhance photosynthesis and respiration rates to the level that temperature and water availability are no longer limiting factors. Changes in photosynthesis and respiration rates would impact net primary production. Our modeled results indicated that the projected annual temperature changes of up to 4 °F would results in higher NPP, but any further increases resulted to lower NPP.

Furthermore, projected increases in temperature and precipitation may influence the potential decay rate associated with each of the litter and soil pools defined in the RHESSys model. Our modeled results indicated that litter carbon and nitrogen pools were simulated to decline due to projected increase in temperature. Also, in general, the rate at which soil organic matter decomposes increases in response to a rise in temperature (Chapman and Thurlow, 1998; Davidson and Janssens, 2006), although rates may then decline after a temperature optimum has been reached (e.g. Fenner et al., 2005). The vegetation primary production and the organic matter decay rate may also increase with rises in temperature to some high threshold temperature point where the adverse effects of higher temperatures will exceed any positive influences on both vegetation and the soil microbial communities (Bassow et al., 1994; Wayne et al., 1998).

Increases in temperature would also decrease soil moisture content which would also influence carbon assimilation.

The impact of individual projected changes for each of climate variables (temperature and precipitation) on the streamflow DOC flux was also studied and presented in figure 3.9. Values for the changes in temperature and precipitation were based on the climate projections described in Chapter Two of the USGCRP report (2009) for Northeastern United States (Table 2.1 and 2.2).

A feedback index (FI) can be used to estimate the extent to which changes in a parameter will influence the DOC flux.

$$FI = (\text{Stream_DOC}_i - \text{stream_DOC}_0) / (i - o) \quad (\text{Equation 3.1})$$

Where the stream_DOC_i is the simulated seasonally/annually averaged stream DOC flux using the changed values for the test parameter, the stream_DOC_0 is the simulated background stream DOC flux using the original values for the test parameter, i is the new value of the test parameter, and o is the original value of the test parameter. A positive FI means larger values of the test parameter will increase the DOC flux and a negative FI means larger values of the test parameter will decrease the DOC flux.

Our simulated annual temperature feedback index results are positive under all scenarios, indicating temperature will have a positive impact and increase the streamflow DOC flux as compared to the 1960-1979-time period. However, the trend toward higher temperatures is negative, meaning higher temperatures do not necessarily increase the streamflow DOC flux even further. As discussed above, even though rises in air temperature may initially stimulate primary vegetation production by accelerating photosynthesis and enhancing vegetation respiration and organic matter decay rates, temperatures may reach a point at which they exceed

the tolerance of vegetation and then they may act as a limiting factor for vegetation growth (Bassow et al.,1994; Wayne et al.,1998). Under these conditions, an increasing temperature will only serve to increase respiration rates and decrease stream DOC flux and concentration. Changes in streamflow DOC flux become more complicated when precipitation estimates alone are changed to be consistent with precipitation projections. As discussed, precipitation is key in explaining changes in the long-term DOC pattern (Hudson et al., 2003). The store of DOC compounds in peaty soils is flushed from the soil by rainfall or snowmelt, with the highest concentrations often coinciding with the higher flow levels (Andersson et al., 1991; Arvola et al., 2004; Worrall et al., 2002; Laudon et al., 2004).As the DOC mass export and runoff are tightly coupled (Dillon and Molot, 2005), it would be expected that higher precipitation would always increase the loss of organic carbon from terrestrial systems (Clair et al.,1994) and lower precipitation amounts the would cause a reduction in export of DOC from terrestrial to aquatic systems (Schindler et al.,1997). However, an increase in precipitation may not always correspond to an increase in the DOC flux because the flux is also influenced by air temperature, and the stored DOC available in the terrestrial or wetlands portions of the watershed. These results can also be explained by the higher correlation of changes in temperature on DOC flux than from changes in precipitation only. Temperature plays a more important role on DOC production and therefore on the availability of DOC for transport within the catchment.

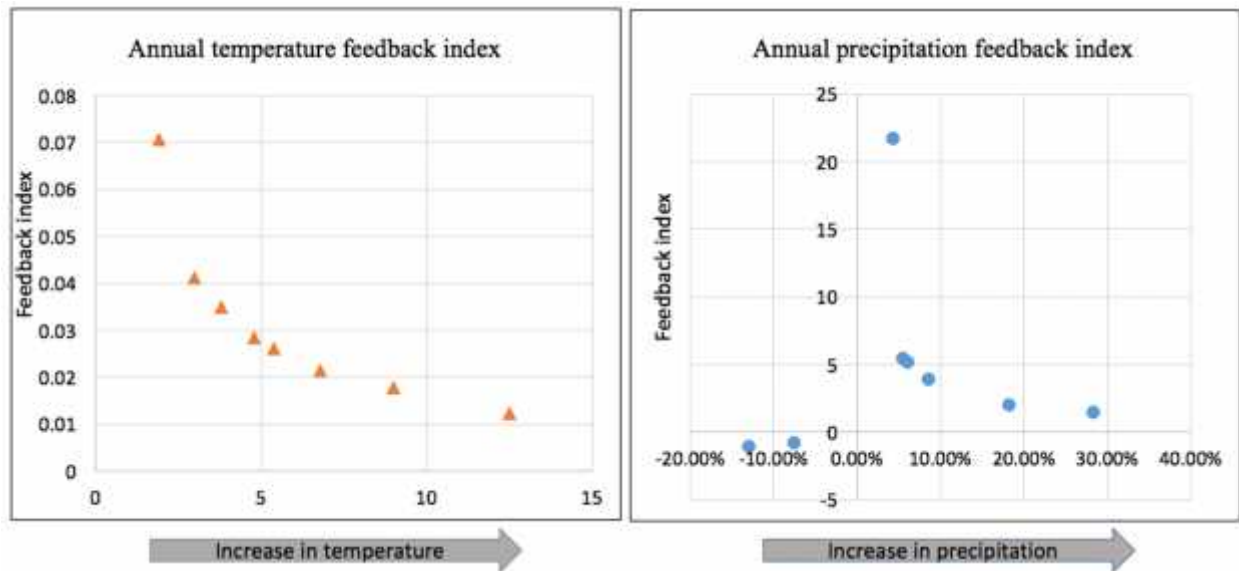


Figure 3.9, Impact of projected temperature and precipitation changes on DOC flux

We also compared the RHESSys simulated seasonal streamflow DOC flux and concentration in the Penobscot Watershed. Figure 3.10, illustrates the seasonal DOC flux (KgC/ha) for the base timeline or past (1963-1972), current (2004-2012), and cumulative result for future projections for mean and very likely range under low and high emission scenarios. Our results indicate an increase in the current winter DOC flux (blue circle) as compared to the 1960s *mean* range under both *low* and *high* emission scenarios and the *very likely* scenario under a high emission scenario. The predicted increase in winter DOC flux is explained by the projected increase in winter temperature which results in earlier and higher streamflow. The springtime DOC flux (green triangles) is simulated to be somewhat lower in the future, which can be explained by increase of winter DOC flux and reduction in DOC availability in spring time and projected simulated decreases in spring time streamflow. These changes in the winter and spring DOC flux also is in agreement with our earlier results in snowmelt timing presented in chapter two. The highest peak of DOC flux generally occurs during snowmelt timing, so any changes in

the timing of snowmelt, would impact DOC export as well. Changes in the winter/spring DOC flux will be discussed later in this chapter. The simulated results do not indicate much of a change in streamflow DOC flux in the summer time (orange triangles). Our modeled summer streamflow results didn't show a statistically significant change since 1960s, however, the projected values are less than current time periods. Even though the summer precipitation, under the *mean* scenario, is expected to slightly increase, the temperature is also expected to increase in the summer. Projected increase in summer may lower the net primary production in vegetation (that was captured by RHESSys model) and may also increase soil evaporation and decrease water availability in the system for the transport of DOC. Furthermore, the Autumn DOC flux (yellow squares) is simulated to slightly increase in future under all scenarios except the *very likely* scenario under low emission for both the *mid-* and *end of century* due to a projected decrease in precipitation. In addition, our simulated projected streamflow results also showed an increase in Autumn streamflow since 1960s but less than current time periods (2004-2012).

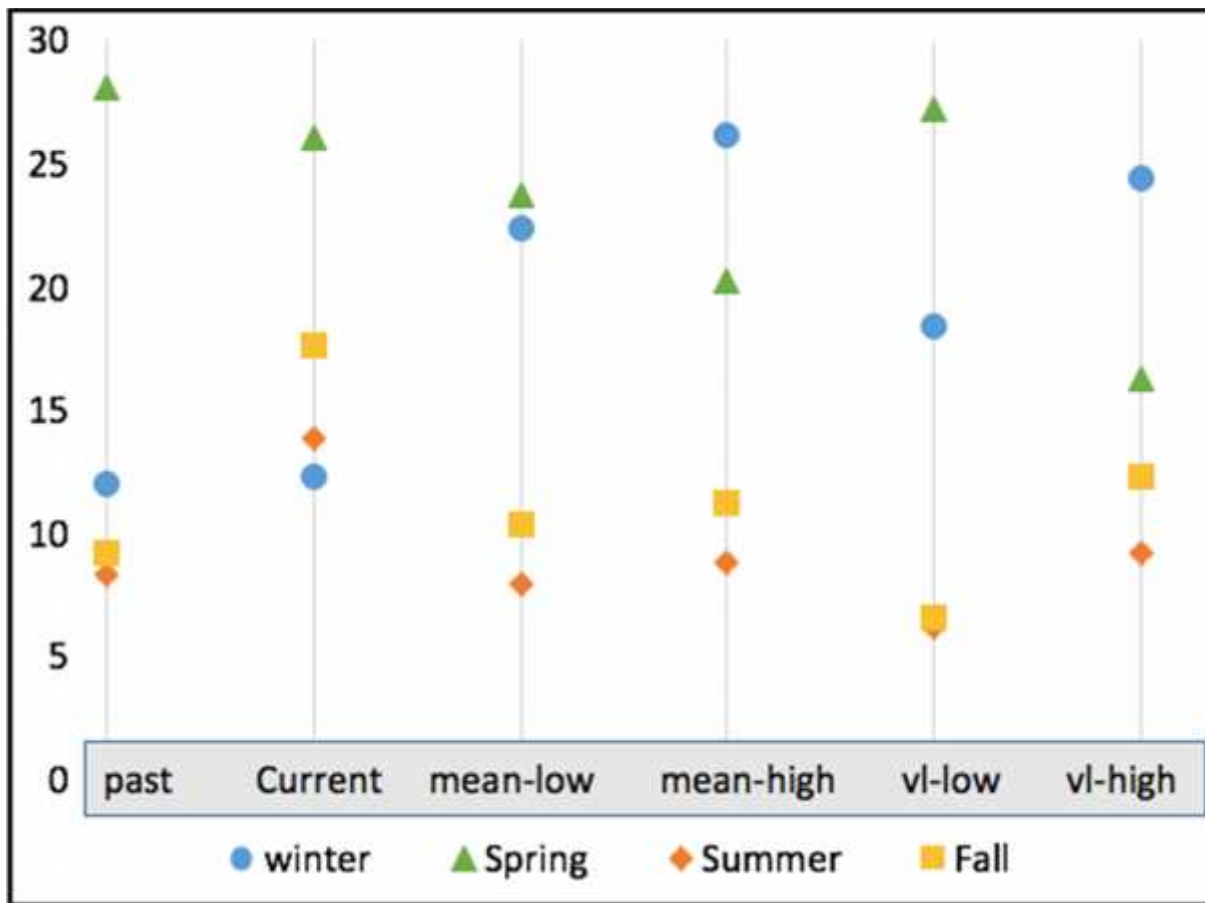


Figure 3.10, The Penobscot Watershed seasonal streamflow DOC flux

We also compared the seasonal DOC concentration values (mg C/lit) in the Penobscot Watershed. Figure 3.11, illustrates the seasonal DOC concentration for the base (1963-1972), and current (2004-2012) timelines, and the cumulative result for the future projections for the *mean* and *very likely* range under the low and high emission scenarios. Our results indicate that while winter DOC flux is predicted to increase under most scenarios as compared to the base time-line (past), the winter DOC concentrations (blue circles) are predicted to decrease for the *mean* range under both the low and high emission scenarios and the *very likely* scenario under high emission scenario. The springtime DOC concentration (green triangles) is simulated to be

higher in the future, which can be explained by an earlier start to the green up season due to the projected increases in temperature and precipitation. The summer time DOC concentration is predicted to increase in the future as compared with base time-line (past). While the summer DOC concentrations (orange diamonds) are projected to increase in future, the predicted values are simulated to be lower than the current time period (2004-2012). This can be explained by the adverse impact of the projected rises in temperature on photosynthesis, decomposition processes and evapotranspiration. Furthermore, the predicted increase in the Autumn DOC concentration (yellow squares) can be explained by increases in the vegetation growing season because of the projected higher temperatures and precipitation for this season.

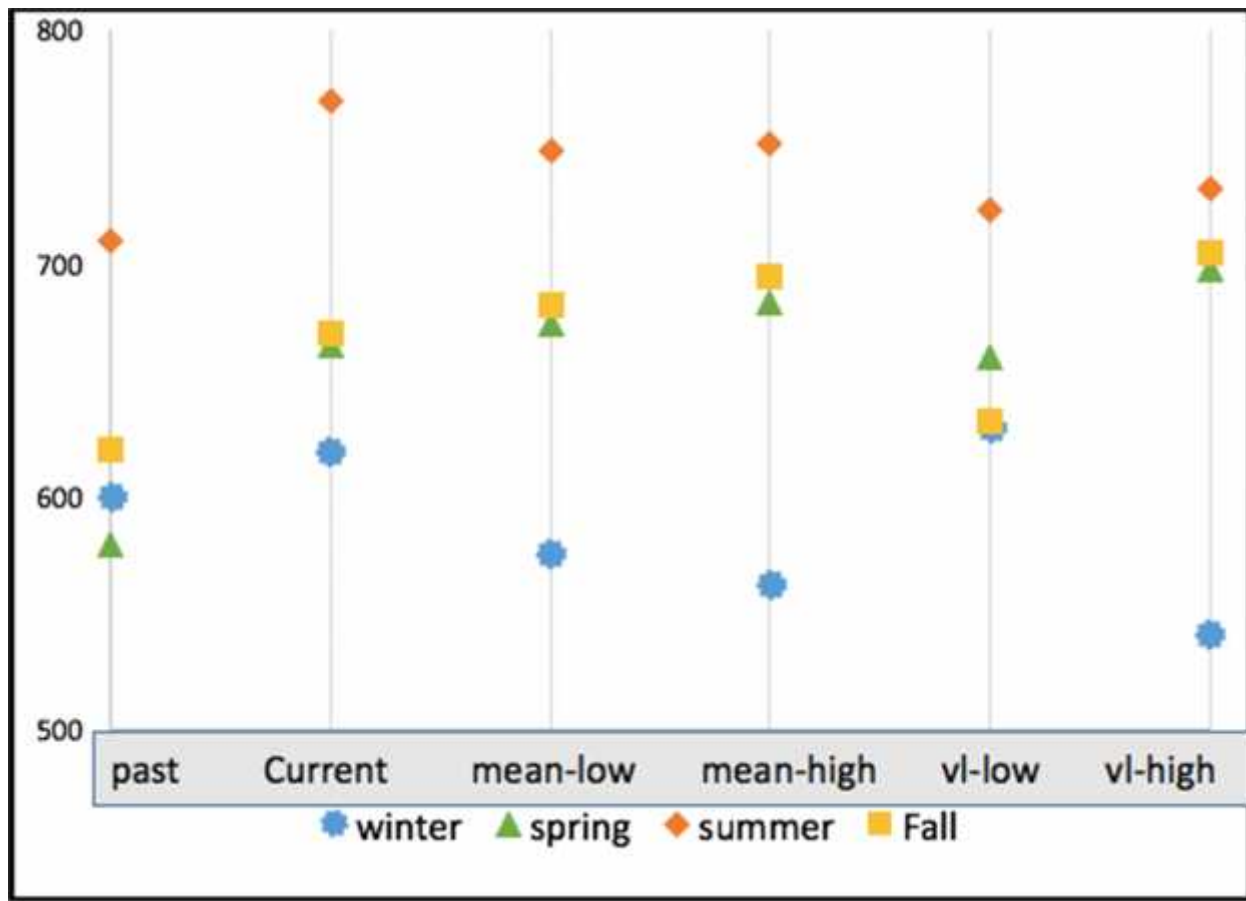


Figure 3.11, The Penobscot Watershed seasonal streamflow DOC concentration

As the highest peak of DOC export into the streams, generally coincide with the snowmelt timing, we further explored changes in the winter/spring DOC flux by using the RHESSys model. The decrease in the amount of springtime DOC flux and the increase in the winter flux may be primarily due to changes in the timing of the snowmelt and increases in winter streamflow while a decline in spring streamflow was observed by our modeled results. Changes in the timing of the snowmelt would result in changes in the timing of the peak DOC release into the stream. Hodgkins et al., (2003) have already shown that an advance in the timing of high spring flows in to the rivers of New England which is presumably related to the timing of the snowmelt. Furthermore, our simulated RHESSys results, along with observed USGS streamflow winter/spring center timing results presented in chapter two, illustrate an earlier shift

in the timing of snowmelt. As noted in chapter two, both the precipitation and temperature values for all the projected climate scenarios, with the exception of the *very likely* scenario under low emissions for the *mid- and end-of-the-century*, are expected to increase in the future.

Winter precipitation in the Penobscot watershed falls mainly as snow and there is little leaching of soil carbon stores during the winter months. Therefore, the projected higher precipitation in the winter time, coupled with higher temperatures, will change the form of winter precipitation in the future, resulting in more rain than snow (Hayhoe et al., 2007). This trend has already been reported in New England, USA for the period of 1949 through 2000 (Huntington et al., 2004). This phenomenon, along with snowmelt timing shifts toward earlier dates may account for the potential increases in winter DOC flux predicted for the future. Figure 3.12 illustrates the average monthly changes for the winter and the spring for the base time line (past, 1963-1972), current (2004-2012) and the mean range under a high emission scenario for both the mid-century (2042-2051) and the end-of-century (2082-2091). Our simulated RHESSys results indicate that the DOC flux is highest in April for the current time period, while our future predicted DOC flux shows that the April DOC flux is predicted to decrease in the future as compare with both the past and current time periods. While our results are showing a decrease in the April DOC flux in future, the March DOC flux is predicted to increase as compared to the past and current time periods. Therefore, this graph also shows that the earlier snowmelt timing, coinciding with the highest peak of streamflow DOC flux, is shifting towards earlier dates, which may well explain the predicted changes for winter and spring DOC flux in the future.

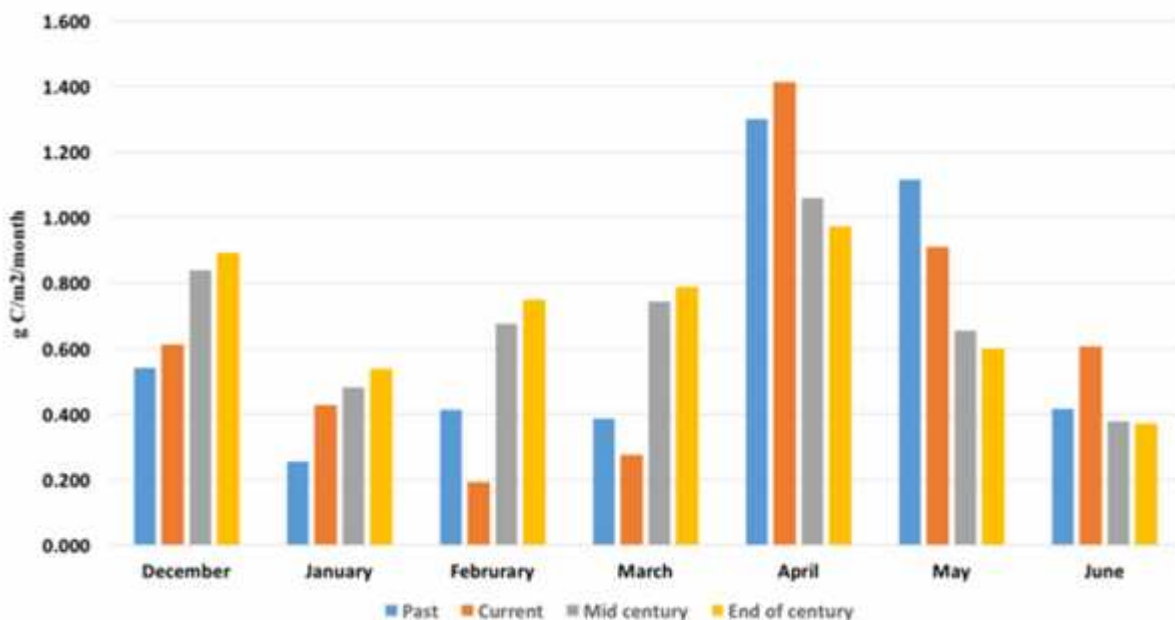


Figure3.12, Average winter and spring DOC flux distribution

3.6. Conclusions

The hydrological transport of dissolved organic carbon between the different pools in an ecosystem appears to be sensitive to potential climate changes in the future. In this study we used the RHESSys hydro-ecological model to simulate the streamflow DOC flux from the Penobscot Watershed into the Gulf of Maine. We also explored the sensitivity of the streamflow DOC flux to future climate projections and investigated the role of temperature change and precipitation change both individually and coincidentally.

The simulated DOC flux and concentration values matched well with the observed data as well as with the regression model LOADEST. However, the more complex RHESSys model provides a better understanding of the within watershed hydrological and ecological processes influencing the DOC flux.

Several sensitivity analyses were done to evaluate the influence of soil parameters (DOM production rate and DOC absorption rate) on the DOC simulation. Our results suggest that increases in the DOM_production_rate, as a soil type specific parameter, will result in the increased conversion of litter carbon into DOC. It should be noted that our modeled results indicated a decline in litter carbon and nitrogen pool as the projected annual temperature exceeds 4 °F that also resulted in lower vegetation NPP.

Transition of the DOC from the terrestrial to aquatic systems is also regulated by the mineral soil absorption which is quite hard to quantify. A negative correlation between the DOC absorption rate and the DOC flux was found in this study.

This study also found that the annual export of DOC was increased under all of the projected climate scenarios in this study as compared with the past time line (1963-1972), with the highest increases occurring in the winter DOC flux. The modeling results indicate some shifts in the annual peak DOC flux. Generally, the annual peak discharge of DOC coincides with the timing of snowmelt, which also is undergoing change itself due to climate change. Therefore, our model results indicate, on average, a decrease in streamflow DOC flux during the springtime under all scenarios.

Projected changes in precipitation and temperature resulted in modeled increases in the streamflow DOC flux in the future although the magnitudes were somewhat different. Changes in temperature were more highly correlated with changes in the future streamflow DOC flux than were changes in precipitation.

All in all, these modeling results demonstrate that future climate change projections will impact the DOC flux and the DOC concentrations in the Penobscot Watershed by affecting both the ecological and hydrological regimes within the watershed.

CHAPTER 4

ASSESSING THE ROLE OF FOREST LAND COVER CHANGE SCENARIOS AND WETLAND LOSS ON STREAMFLOW DOC FLUX AND CONCENTRATION

4.1. Introduction

4.1.1. Forest land cover change scenarios

Carbon is cycled and recycled through the atmosphere, ocean, and soil and is incorporated in to the life cycles of plants and animals. Carbon sequestration and release varies between forest types. On average carbon stocks are higher in Tropical forests followed by Temperate forests and Boreal forests (Intergovernmental Panel of Climate Change, 2007). However, as a result of climate change, forest carbon cycling behavior may well change as a response to elevated atmospheric CO₂, and varying temperature and precipitation patterns. These climatic changes may affect forest species composition and species specific carbon allocation strategies, thereby affecting the amount of carbon that goes into stems, leaves, and roots. Differences in allocation and the rates of decomposition for different species litter components may well affect the rate of DOC flux.

Quantifying forest carbon fluxes and dynamics helps us to have a better understanding of interactions between the atmosphere, forest, and soil, and the responses to climate and land cover

change. This study focuses on an understanding of how changes in the forest land cover and wetland abundance in a watershed may affect streamwater DOC concentration and fluxes in response to changes in forest carbon cycling.

Observations and simulations have both been used to study terrestrial carbon storage and flux in previous studies. In some studies, the Eddy covariance direct observation technique has been used to estimate carbon, water and energy fluxes between an ecosystem and the atmosphere through the establishment of an international network of Flux towers. Eddy covariance measurements can not only be used to inter-compare multiple biomes (Keenan et al., 2013), but also can be used for calibration and/or validation of terrestrial ecosystem models (Baldocchi, 2003 and Burba G, 2013). In addition to these direct measurement tools, empirical and process-based models have also been developed for use in the large-scale simulation and forecasting of carbon fluxes. Inherent soil parameters like the C:N ratio (Aitkenhead and McDowell 2000) or Chromophoric Dissolved Organic Matter (CDOM) as a component of DOC, can be used as a proxy of DOC flux (Bissett et al., 2001; Bricaud et al., 1981; Chen 1999; Chen et al., 2002; Green and Blough 1994; Huang and Chen 2009).

The Load Estimator (LOADEST) regression software (Runkel et al., 2004) and the SPATIALLY Referenced Regressions On Watershed attributes (SPARROW) model (described in Chapter 1) are two major empirical models that have been used to simulate carbon and nutrient fluxes within watersheds. A landscape mixing model (Ågren et al., 2013) and decomposition models (DocMod, Currie and Aber, 1997) have also been used to predict DOC concentrations and litter production as components of the carbon cycling through the ecosystem. The process based Biome-BGC (Running and Hunt Jr., 1993) (which forms a major component of the RHESSys model) has been widely used to simulate the storage and flux of water, carbon, and

nitrogen within the vegetation, litter, and soil of unmanaged terrestrial ecosystems. The Biome BGC model is designed to simulate detailed forest processes as well as the response of these processes to climate and land cover variations. The conceptual framework of the carbon cycle in plants needs to be defined in such process based models. As described previously for RHESSys, ground information (streamflow and climate data), input maps (vegetation, soil, land cover, DEM) and physiological parameters (species specific vegetation parameters) as well as soil physical parameters need to describe. In addition, the accurate calibration of these parameters and an evaluation of the validity of the resulting model are important aspects of any such modeling study.

In this chapter, we used RHESSys to simulate the streamflow DOC fluxes from the large Penobscot Watershed into the Gulf of Maine, focusing particularly on differences in the amount of DOC flux and concentration coming from coniferous and deciduous dominant watersheds. RHESSys combines several sub-models, including the ecosystem process model (Biome-BGC), with spatially explicit meteorological information from the MTCLIM model (Running et al., 1987) and two hydrologic routing models; TOPMODEL (Beven and Kirkby, 1979) and the Distributed Hydrology Soil Vegetation Model (DHSVM, Vigmosta et al., 1994) to make spatial and temporal predictions of carbon, water, and nitrogen dynamics over landscapes (more information about these sub-models can be find in chapter one, chart 1.1).

The fixation of carbon in RHESSys starts with photosynthesis and the maintenance of respiration. Carbon is then allocated to different vegetation tissues based on fixed allocation ratios. The vegetation allocation strategies are influenced by the functional traits of specific species to maximize plant growth as well as achieve an optimal level of metabolic activity.

In trees, growth adds biomass as foliage, wood and roots (Schulze and Chapin 1987; Stitt and Schulze 1994). However, there is a limit on carbon assimilation since there is a limit in leaf development due to a maximum possible leaf area, leaf orientation and the availability of light (Monsi and Saeki, 1953). There is also a limit for growth determined by the balance of assimilation and respiration.

In the RHESSys model, the carbon and nitrogen in plant, litter and soil components are linked and the turnover rates of vegetation components (e.g. fine roots, leaves and stem woods) are linked with their corresponding litter pools. Generally, leaf life span is an important plant characteristic associated with the species and the ecosystem processes. Differences in life span affect carbon cycling by directly impacting the leaf/needle turnover rate. Annual foliage turnover rates, along with leaf physiological traits, regulate the carbon cycling by effecting the gross primary production and net carbon export.

The turnover ratios for fine roots, leaves, and stem woods are defined for each species specifically in the vegetation default file (as an input for RHESSys). To control the balance, some parts of the plant tissues die and are either shed as a litter or retained as heartwood. Decomposition of litter or humus will lead to the transport of dissolved carbon into nearby streams and into the groundwater. Decomposition base rates are considered for each of the litter pools and soil pools defined in the model and then can be adjusted by soil temperature, nutrient availability and soil water.

In addition to physiological factors, as has been shown, the stream DOC simulation is largely influenced by the hydrological cycle. RHESSys simulates vertical and lateral soil moisture for each patch object. Vegetation specific characteristics, such as their ability to hold snow and water, can impact the amount of precipitation that reaches the soil surface after

interception by vegetation. The rate of transpiration varies by the vegetation specific maximum stomatal conductance and additional environmental factors such as light, ambient CO₂ concentration, leaf water potential and vapor pressure deficit which impact soil moisture content.

A three-layer model (root zone-unsaturated and saturated zone) accounts for vertical fluxes in RHESSys after throughfall reaches the soil. The water table dynamics between these layer along with the distribution of DOC with depth and DOC absorption rate controls the amount of DOC leach out to stream.

Changes in climate and the impact of extreme weather events, wildland fires, insect infestation, harvest activities, and forest diseases are all important drivers of vegetation change in forests and can influence changes in carbon stocks and fluxes by changing forest species composition, growth, and productivity (Soja et al., 2007, Schapphof et al., 2016). Changes in climate (temperature and/or precipitation) have already been impacting the carbon cycle across United State. A few recent studies, based on eddy-covariance measurements, have indicated that some boreal forest areas may be in transition from C-sinks to C-sources, likely due to the thawing of permafrost under climate warming, that may release large amounts of carbon (Dolman et al., 2012, Gauthier et al., 2015). Studying temporal and spatial changes in DOC export can help us to understand terrestrial carbon cycling and to detect any shifts from carbon sink to carbon source or visa versa in northern latitude forested ecosystems. Net Ecosystem Exchange (NEE) can also be used to estimate the net exchange of CO₂ between atmosphere and terrestrial system. The tree species composition of the northeastern North American forests has already begun to shift slowly in response to climate (Jackson et al., 1997; Williams et al., 2004). Future climate projections about the forests of the Northeast of United States and Eastern Canada

indicate a reduction in suitable habitat for spruce-fir forests (Conifer) and an expansion of oak-dominated forests (Deciduous) (Rustad et al., 2014).

Changes in climate and land cover would result in forest vegetation composition change, influencing carbon stocks or fluxes by altering species, growth rate, and productivity. The Northeastern American forest vegetation composition has already begun shifting as a response to ongoing changes in climate. Our comparison also depicts an increase in conifer trees in the northwest and western parts of the State and a loss in both mixed and deciduous forests in the southern half of the State. In order to explore the impact of potential projected scenarios of forest composition change, we have considered four progressive forest vegetation changes to encompass both conifer dominance and/or deciduous dominance in the State of Maine in the future. We seek to understand how changes in the proportions of forest vegetation types will affect changes in the amount of streamflow DOC flux and concentration from the Penobscot Watershed into the Gulf of Maine. We were interested in studying how changes in forest species composition may affect forest growth and the production of biomass that is decomposed to generate DOC as well as the impact on evapotranspiration rate, throughfall (the amount of precipitation reaches the ground from vegetation canopy cover), streamflow and baseflow regulating the fluvial DOC transport. Thus the goal is to have a better understanding of the inter-annual variations in streamflow DOC flux and concentration that would occur if the Penobscot Watershed forested land cover type was changed into more of a conifer-dominant or more of a deciduous-dominant land cover.

4.1.2. Wetland loss scenarios

Wetlands generally are considered as carbon sinks in their ability to provide an optimum habitat for carbon sequestration and the long term sequestration of carbon from the atmosphere.

Wetlands have unique natural characteristics which result in the storage of carbon, the maintenance of water quality in rivers (water purification), the regulation of flows (helping to reduce the impact of storm damage and flooding), the recharge of groundwater, and the provision of habitats, as well as contributions to tourism and recreation services. Wetlands are estimated to cover approximately 9% of the planet's land surface (Ramsar Scientific and Technical Review Panel, 2007) and contain 35% of the global terrestrial carbon storage.

There are previous studies that have shown that wetlands, in particular, play a very important role in DOC concentration and flux per unit watershed area (Creed et al., 2008; Huntington and Aiken, 2013) and that tributary DOC concentration and flux are positively correlated to the percentage wetland area in a catchment.

Photosynthesis and the accumulation of organic matter in soils, sediments and plant biomass all contribute to carbon sequestration in wetlands. Wetland plants generally grow at a faster rate rather than they decompose, resulting in a net accumulation or sequestration of carbon over time. The unique hydrologic conditions in wetland soils have a major impact on biogeochemical cycling.

Wetland soils are well saturated with poor drainage and a high water table. The lack of oxygen (anaerobic conditions) that results from soil saturation causes the organic material to build up in the soil more rapidly than it decays because the decomposition rates are slower under anaerobic conditions. This results in the development of a thick organic layer under continuous soil saturation. "The combination of elevated water tables, high productivity, and lower decomposition has led to significant carbon storage in these soil types, especially in high latitude wetlands" (Gorham, 1991). If these wetland soils are drained or exposed to the air; aerobic

decomposition of organic matter, which is much faster than anaerobic decomposition, will occur, resulting in net losses of organic matter and, potentially increasing DOC export.

Therefore, the degradation of wetlands is a significant source of carbon dioxide emissions to the atmosphere. In addition, wetlands can act both as a carbon sink by trapping carbon-rich sediments from catchments or as a source by releasing carbon through water flow into floodplains. These switches can be a natural process due to seasonal or climate change factors or can be affected by human management (land cover change).

Encouraging wetland protection and restoration for carbon storage offers large environmental advantages. Increases in soil organic carbon from carbon sequestration in wetlands can improve water and nutrient holding capacities in the soil which can lead to better water quality by decreasing nutrient runoff into surface and ground waters.

The role of wetlands in carbon storage or carbon dioxide and methane emission in the future is uncertain and needs more investigation as the processes involved are very complex. Since wetlands can act as both sources and sinks of carbon, the feedback of wetlands upon climate and land cover change in the future depends on how carbon storage and fluxes may depart from the historical trends. Environmental and land cover changes that influence the abundance of wetlands will likely impact the magnitude of streamflow DOC transport from watersheds to coastal areas. Since wetlands are very vulnerable to changes in the quantity and quality of their water supply, climate change may impose a significant effect on wetlands, especially by altering their hydrological regimes. (Erwin, 2008).

Forested wetlands, scrub-shrub wetlands, and emergent wetlands are three types of wetlands in State of Maine. Forested wetlands are wetlands dominated by woody vegetation 20

feet or taller. They are often seasonally flooded but they don't have water year-round. Cedar swamps, spruce bogs, red maple fens, and silver maple floodplain forests are also common types of forested wetlands in State of Maine. Scrub-Shrub Wetlands are dominated by woody vegetation with less than 20 feet in height such as alder thickets, black spruce peat bogs, huckleberry bogs and sweetgale fens. Common types of emergent wetland in Maine are represented by Bullrush marshes, tidal marshes, saltmarshes, open-water marshes, and sedge meadows.

Wetlands occupy about 12% of the land area in Maine; 61% of these wetlands are forested, and the remainder are shrub, emergent vegetation, or un-vegetated (Armstrong, 1996). In this research, we explored the role of wetlands in the fluvial export of DOC from the Penobscot Watershed into the Gulf of Maine by manipulating the wetland abundance based on the input wetland maps created from wetness index parameters and elevation. In order to study the sensitivity of the Penobscot Watershed to a loss of wetland areas, an incremental increase in the loss of wetland areas was studied. We then used another explicit method to look at the impact of wetland loss on amount of DOC flux by using ARC GIS as a tool to shrink wetland areas. This study helps us to have a better understanding on the role of wetlands in carbon cycling in a catchment.

4.2. Methodology

4.2.1. Forest land cover change

The forest vegetation types of the Penobscot Watershed are an assemblage of mixed forest (conifer and deciduous), conifer alone, and deciduous alone. Red maple, spruce, sugar maple, yellow birch and white pine are the most dominant vegetation types in that area. The

impacts of four progressive forest land cover changes on the streamflow DOC fluxes and concentration from the Penobscot Watershed into the Gulf of Maine were explored. Table 4-1, represents the progressive forest species composition changes. For the first and second scenarios, coniferous vegetation type dominance was assumed in the future. A progressive forest species change was implemented that looked at the extent to which coniferous areas would remain coniferous, while deciduous areas would be converted to mixed forest, and mixed forest areas would be replaced by coniferous types in the first scenarios. In the second scenario (following the first scenario) all the forest type vegetation was assumed to be converted to conifers (100% conifers). Then, a progressive forest species composition change towards deciduous type dominance was explored in the third and fourth scenarios. For the third scenario, coniferous areas in original land cover were replaced by mixed types, and mixed types were replaced by deciduous types, while deciduous areas remained constant. In the fourth scenario, (following third scenario), all the forest type vegetation was replaced by deciduous trees (100% deciduous). These various studies can be used to better understand the role of vegetation types in fluvial DOC export. The percentage of each forest type in each scenario is represented in table 4.1.

Table 4.1, Progressive forest species composition change

Forest vegetation Types (Original)	Conifer Dominancy		Deciduous Dominancy	
	Mixed-Conifer	Conifer	Mixed-Deciduous	Deciduous
Conifer	Conifer	Conifer	Mixed	Deciduous
Deciduous	Mixed	Conifer	Deciduous	Deciduous
Mixed	Conifer	Conifer	Deciduous	Deciduous
C(31.3%)	C (79.7%)	C (100%)	M (31.3%)	D (100%)
D (20.3%)	Mixed (20.3%)		D (68.7%)	
M(48.4%)				

4.2.1.1. Model parameterization

The worldfile defines the landscape representation within RHESSys, and it is created through a GRASS (Geographic Resources Analysis Support System) interface software program. It references the input maps and a text document defining the initial state variables (the template file). These initial state variables correspond to the definition files that describe the characteristics of the variables associated with each level of the spatial hierarchy. The definition parameters values are defined based on literature reviews and they stay constant through time. Table 4-2, shows the parameters for three types of forest vegetation in the Penobscot Watershed.

Table 4.2- RHESSys model vegetation parameterization

Physiological parameters	Vegetation types			Unit	Source
	Deciduous	Conifer	Mixed		
Leaf C:N	25	42	32	KgCKgN-1	White et al. (2000)
Litter C:N	55	93	70	KgCKgN-1	White et al. (2000)
Fine root C:N	48	58	52	KgCKgN-1	White et al. (2000)
Live wood C:N	50	50	50	KgCKgN-1	White et al. (2000)
Leaf litter labile proportion	0.38	0.31	0.34	%	White et al. (2000; Hobbie (1996)
Leaf litter cellulose proportion	0.44	0.45	0.45	%	White et al. (2000; Hobbie (1996)
Leaf litter lignin pool	0.18	0.24	0.21	%	White et al. (2000; Hobbie (1996)
Fine root labile proportion	0.34	0.34	0.34	%	White et al. (2000; Hobbie (1996)
Fine root cellulose proportion	0.44	0.44	0.44	%	White et al. (2000; Hobbie (1996)
Fine root lignin proportion	0.22	0.22	0.22	%	White et al. (2000; Hobbie (1996)
Allocation				kg C kg C-1	
New fine root C to new leaf C ratio	1.2	1.4	1.3	Unitless	White et al. (2000)
New stem C to new leaf C ratio	2.2	2.2	2.2	Unitless	White et al. (2000)
New live wood C to new total Wood C	0.16	0.071	0.1	Unitless	White et al. (2000)
Water interception coefficient	0.045	0.045	0.045	Wint LAI-1day-1	White et al. (2000)
Percent of leaf N in Rubisco	0.088	0.033	0.05	%	White et al. (2000)
Turnover ratio					White et al. (2000)
Leaf and fine root turnover	1	0.26	1	1 yr-1	White et al. (2000)
Live wood turnover	0.7	0.7	0.7	1 yr-1	White et al. (2000)
Specific Leaf Area (SLA)	32	8.2	20	m2 kg C-1	White et al. (2000); Barlett et al (2011)

The values for Mixed forest utilize the mean values for conifer and deciduous

4.2.1.2. Vegetation ecological and hydrologic control on streamflow DOC flux

Differences in inherent vegetation characteristics impact carbon cycling, and differences in the ecological and hydrological processes can affect the amount of DOC that leaches out from

the soil into the watershed streams (such as the rate of evapotranspiration, baseflow and streamflow and net primary production rate). The species characteristics impact the decomposition rate through differences in the proportion of the litter pools as defined in RHESSys model (Labile, Cellulose, Shielded cellulose and lignin).

Pearson correlation analysis was used to examine relationships between simulated streamflow DOC flux and evapotranspiration and the results are presented in figure 4.1. Our modeled results indicate a negative correlation between the daily evapotranspiration rate and the daily fluvial DOC export, indicating that rises in evapotranspiration (e.g. during summer time or due to a rise in temperature) would decrease streamwater DOC (P-value < 0.05, $r = -0.21$). Also, it should be noted, that a strong positive correlation exists between the streamflow and the DOC flux and the baseflow and the DOC flux.

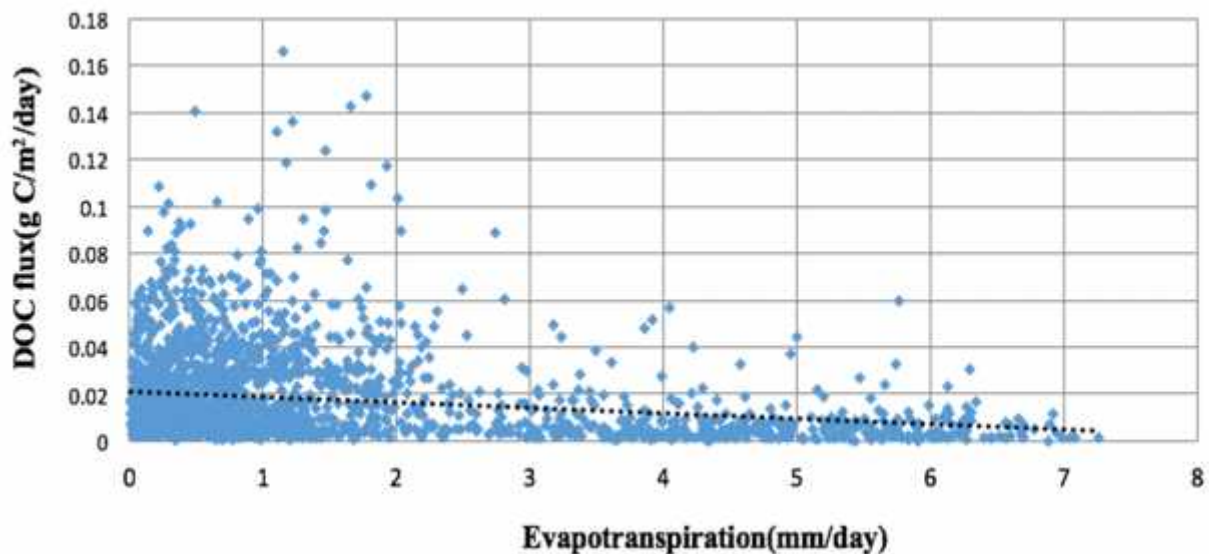


Figure 4.1, The correlation between daily evapotranspiration and daily streamflow DOC flux

4.2.1.3. Sensitivity analysis

The estimation of canopy photosynthesis and respiration, the allocation of net photosynthesis to leaves, stem and roots, plant turnover, along with litter and soil decomposition and respiration estimations are all incorporated in the carbon cycling dynamics captured by the RHESSys Model. Standard parameters for vegetation types such as conifer, deciduous, grass, shrub, wetland, as well as specific soil type parameters are input to the model. Terrestrial export of DOC depends on the net primary production (NPP) of the terrestrial system, the plant material degradation to DOC in the soils (Thurman, 1985), and the hydrological flushing of this DOC to surface waters (Hope et al., 1994; Laudon et al., 2004). In this study, we investigated the role of conifer and deciduous vegetation types on the DOC flux and DOC concentration of the Penobscot Watershed by considering their specific physiological role and their impact on the hydrologic cycle. Figure 4.2 and 4.3 illustrates the correlation between Net Primary Production (during the growing season) and the DOC flux and concentration respectively using Pearson correlation. A positive correlation exists between NPP and the DOC concentration (P-value < 0.05, $r=0.35$) and DOC flux (P-value < 0.05, $r=0.26$). It should be noted that Correlation between monthly NPP and the DOC flux (P-value < 0.05, $r: 0.38$) and the DOC concentration (P-value < 0.05, $r: 0.52$) is higher than daily time series.

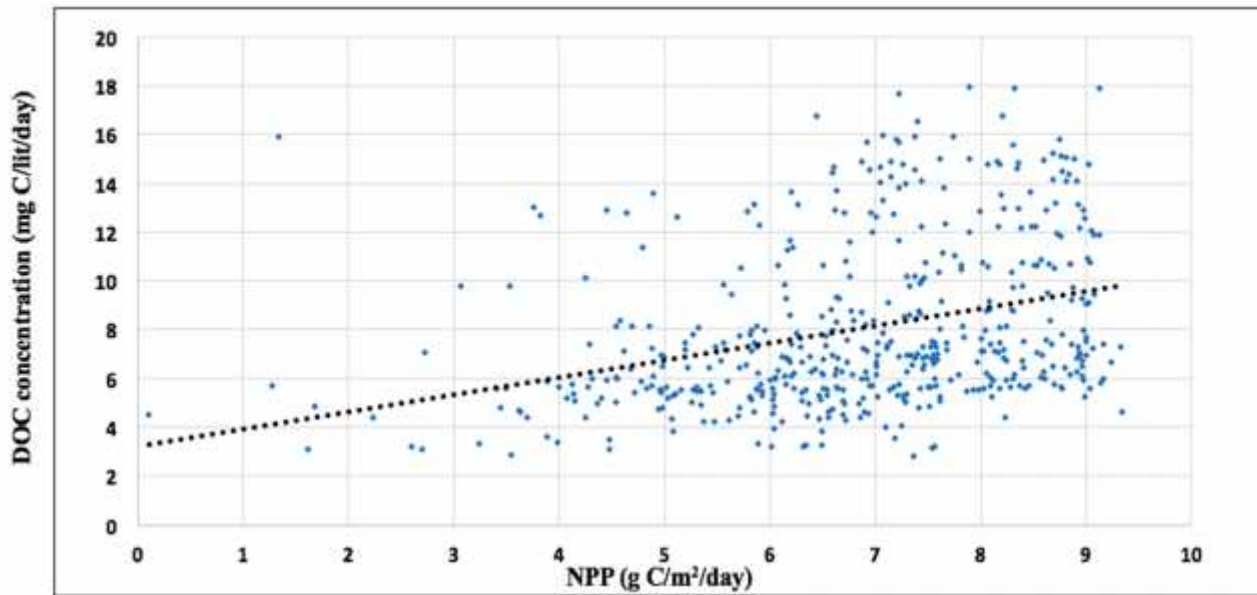


Figure 4.2, The correlations between daily NPP and daily DOC concentration (Growing season)

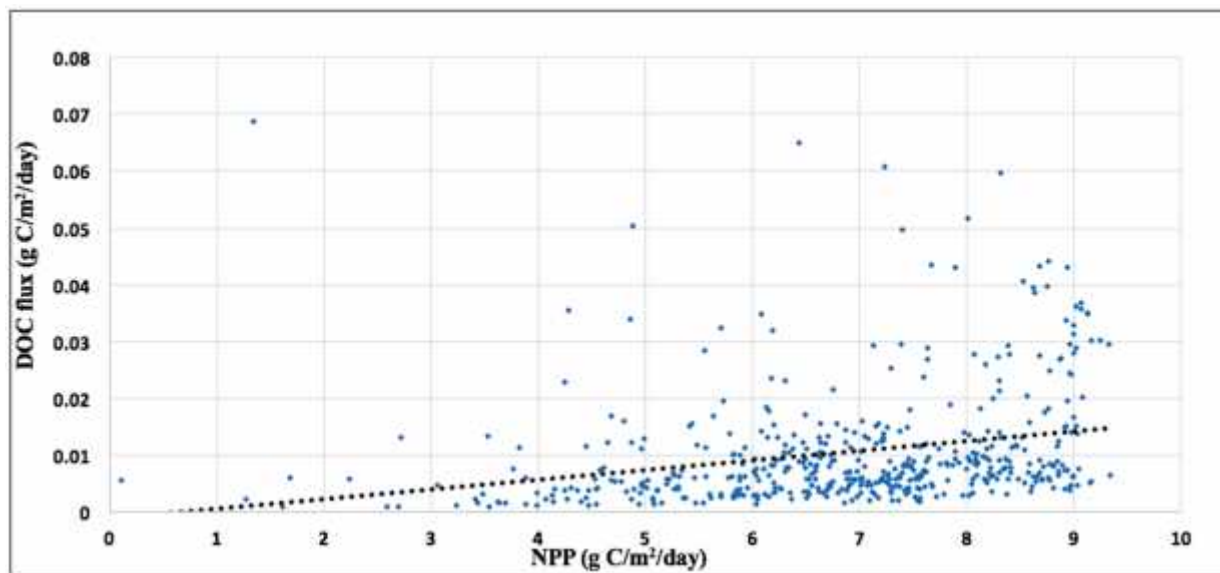


Figure 4.3, The correlations between daily NPP and daily DOC flux (growing season)

As Net Primary Production (NPP) is one of the parameters controlling the amount of terrestrial DOC flux and concentration, we evaluated a few parameters (Leaf C:N ratio, Root C:N ratio, leaf Area Index (LAI) and new fine root carbon to new leaf carbon allocation) that are known to have the highest impact on NPP estimation. The sensitivity of the predicted average annual NPP to variations in the parameter level of -25% to +25% (5% interval) of the vegetation standard value was tested for each such parameter. The variations for each parameter level were tested from the parameterized value for Mixed forests. Furthermore, we performed another set of sensitivity analyses on the parameters that have the highest impact on streamflow DOC flux such as litter C:N ratio and the percentage of litter labile portion.

Vegetation specific carbon to nitrogen ratios define the nutrient requirements for new growth, respiration, photosynthesis and litter production and quality. In this research, we looked at RHESSys sensitivity NPP rate to forest species composition. Figure 4.4, shows changes in leaf C:N ratio representing either deciduous or conifers on NPP rate. Our modeled results indicated that NPP decreased approximately linearly when leaf C:N ratio was increased from optimum value for mixed forest to 25%. NPP also slightly increased when the leaf C:N ratio decreased from optimum value for mixed forest to -15%, when decreased slightly with progressive decreases in the leaf C:N ratio. Therefore an increase in the C:N ratio would decrease NPP by producing a nitrogen limited environment which affects the fraction of nitrogen needed for photosynthesis. It should be noted that conifers have a higher C:N ratios than do deciduous trees.

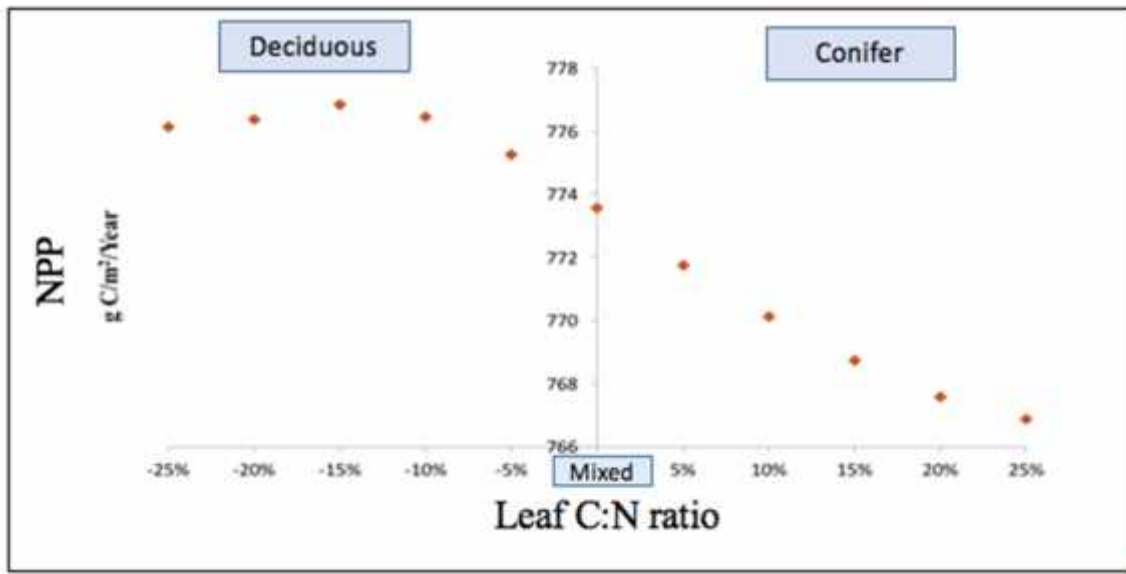


Figure 4.4, Annual NPP changes with changes in Leaf C:N ratio

Figure 4.5, shows changes in root C:N ratio representing either deciduous or conifers on the NPP rate. Our modeled results illustrate that, unlike the leaf C:N ratio, the root C:N ratio has a positive impact on NPP by making more nitrogen available for investment in leaves. Higher ratios of root C:N in deciduous trees result in linear increase in NPP rate.

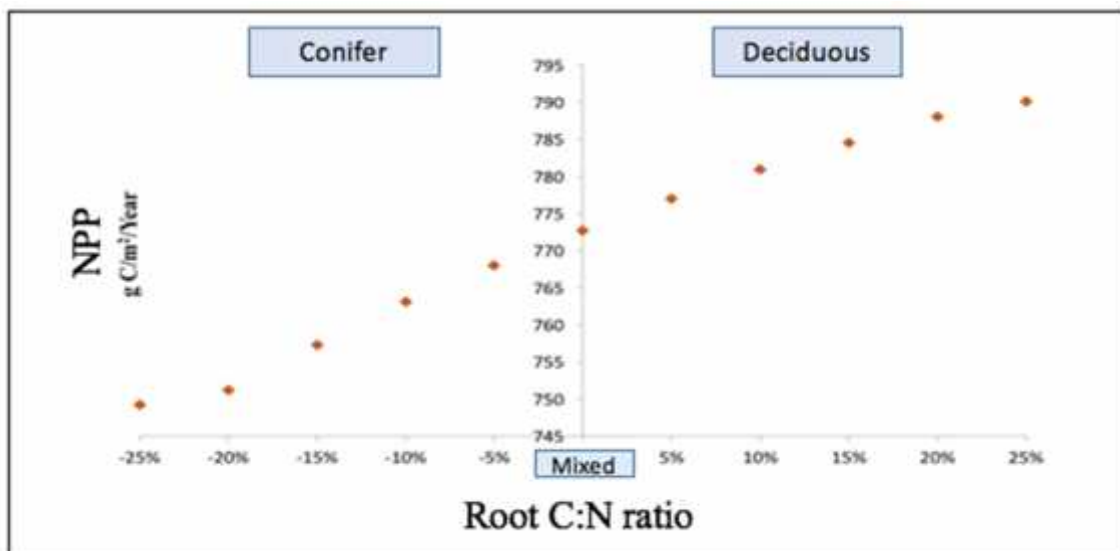


Figure 4.5, Annual NPP changes with changes in Root C:N ratio

Other parameters controlling NPP and therefore available carbon for allocation into plants components are Specific Leaf Area (SLA) and Leaf Area Index (LAI). SLA represents the ratio of leaf area to dry mass. Leaf Area Index (LAI) is one of the key variables related to carbon, water and nutrient cycles in terrestrial ecosystems. Species with high SLA and leaf nitrogen content usually show high potential relative growth rates (Hunt and Cornelissen, 1997). Photosynthetic capacity is positively correlated to both leaf nitrogen content and SLA (Porter *et al.*, 1990; Reich *et al.*, 1994, 1997).

Figure 4.6, shows the impact of LAI changes on NPP rate. Even though higher NPP is usually expected from species with higher SLA and LAI, in times of water limitation, this may result in NPP reduction. In our study area, higher LAI values in deciduous forest resulted in lower NPP rate indicating water limitation may exist under total deciduous dominance. LAI, also controls radiation absorption, interception, photosynthesis, and litter inputs. Generally, deciduous trees have higher LAI and net canopy assimilation rates (Buchmann and Schulze 1999) than do conifers.

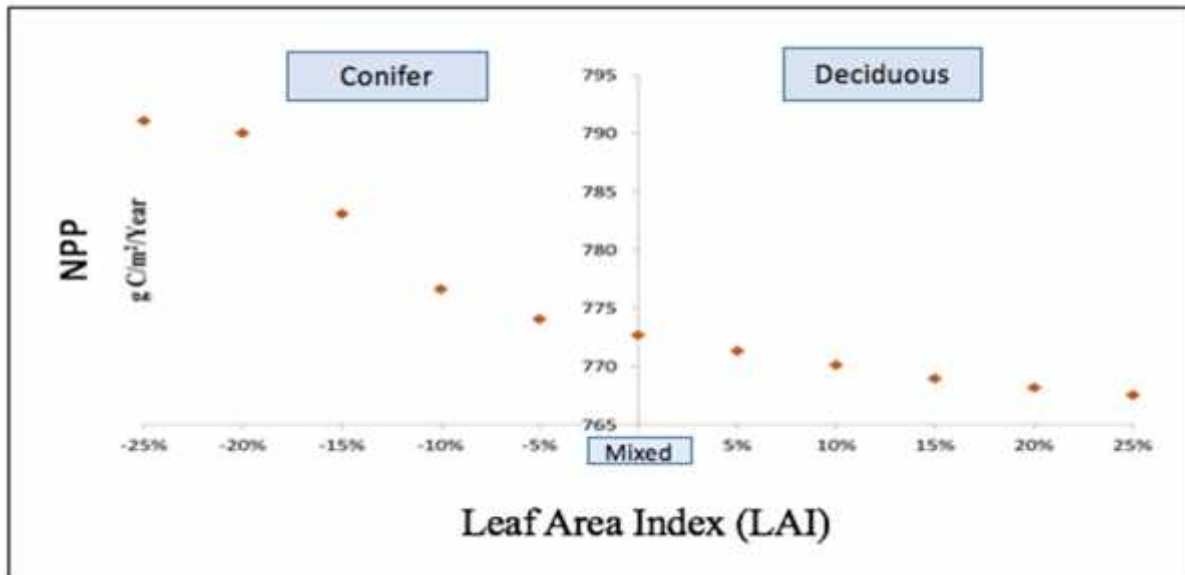


Figure 4.6, Annual NPP changes with changes in Leaf Area Index (LAI)

Net primary production represents the available carbon for vegetation allocation into plant component parts (Leaves, stems and roots) as well as reproduction and defensive compounds. Vegetation specific allocation strategy follows a set of allometric parameters defined in vegetation default file as an input to RHESSys model. One of the parameters that have controlling impact on NPP rate is the proportion of new fine root carbon to new leaf carbon. Figure 4.7, represents the role of new fine root carbon to new leaf carbon change on NPP rate. Our modeled results indicated that higher ratio of carbon allocated in new fine roots and in new leaves in deciduous forests leads to higher rates of NPP. Increased new fine root carbon to new leaf carbon allocation diverts carbon from leaves into roots and would result in lower LAI and therefore lower NPP.

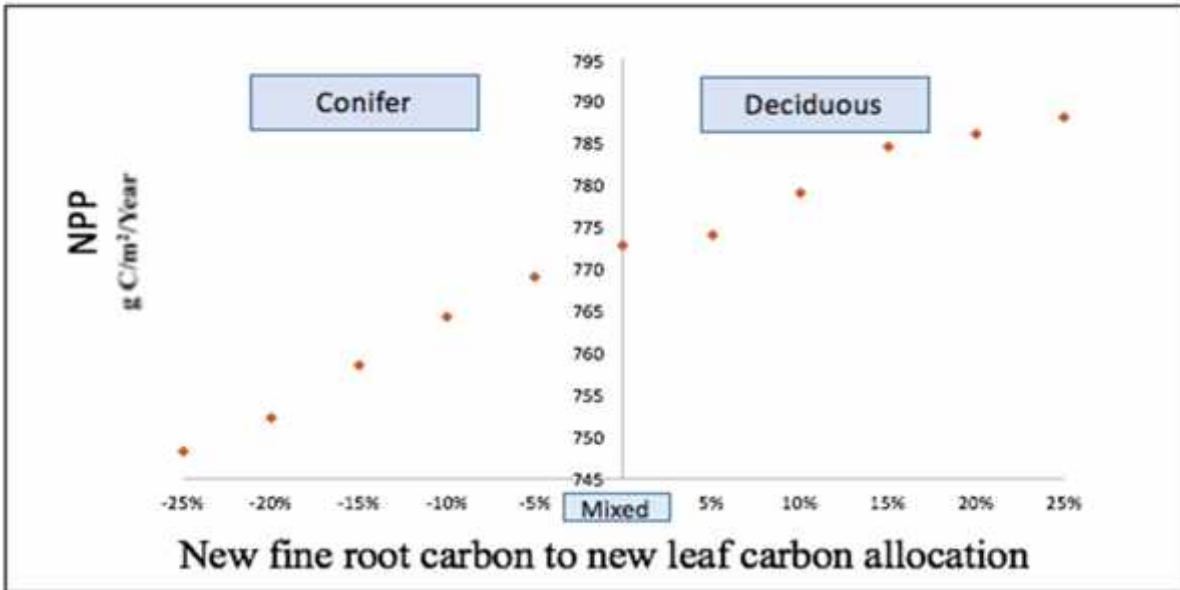


Figure 4.7, Annual NPP changes with changes in new fine root carbon to new leaf carbon allocation

While, leaf and root C:N ratios may impact the net primary production, leaf litter is the major source of DOC and DON, so the litter C:N value is important for estimating DOC and DON export. Figure 4.8, shows average daily streamflow DOC flux changes with changes in the litter C:N ratio. Our modeled results indicate a negative feedback between leaf litter C:N changes and DOC export (supported by Yang, 2013 and White et al., 2000). The negative feedback can be explained by the loss of nitrogen as DOM from leaf litter degrades into DOC and DON. Lower litter C:N ratio in deciduous forests results in higher streamflow DOC flux than conifer forests.

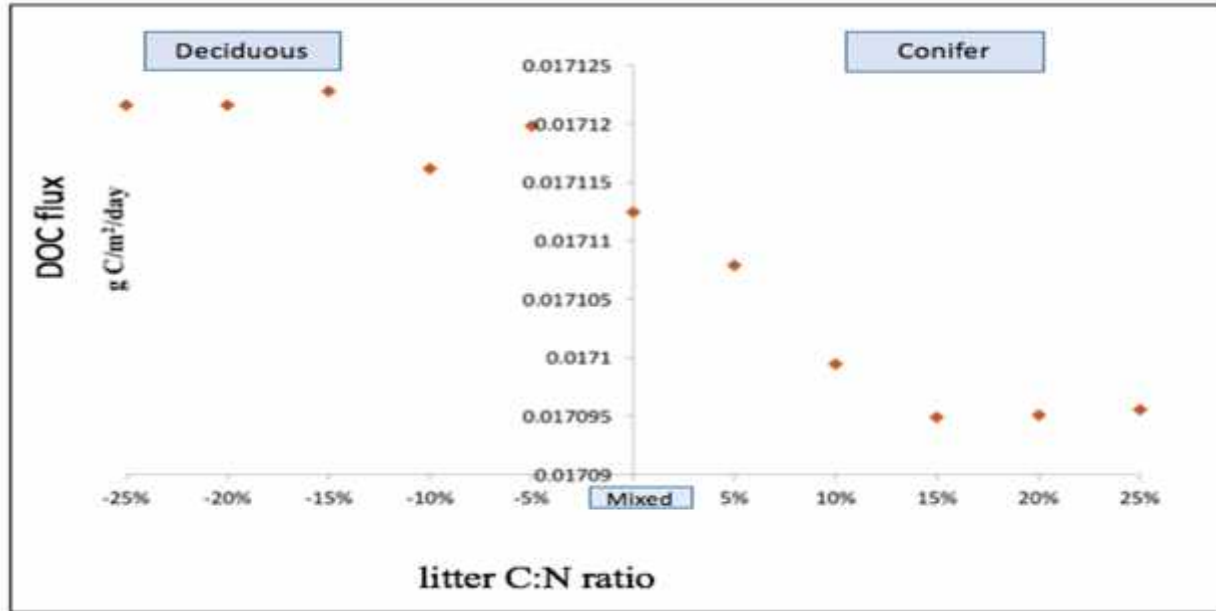


Figure 4.8, Daily streamwater DOC with changes in litter C:N ratio

Leaf litter quality also has an impact on decomposition rates (Berg, 1986; Aber et al., 1990). The percentage of lignin, cellulose, and labile material in fine roots, litter, and dead wood controls the decomposition rates. An increase in the decomposition rate results in more plant material degrading to DOC in soils. Figure 4.9, illustrates the average daily streamwater DOC changes with the percentage of the litter labile portion in vegetation. Our modeled results indicated that a higher proportion of litter labile occurs in deciduous forests than in conifers and results in higher streamwater DOC flux.

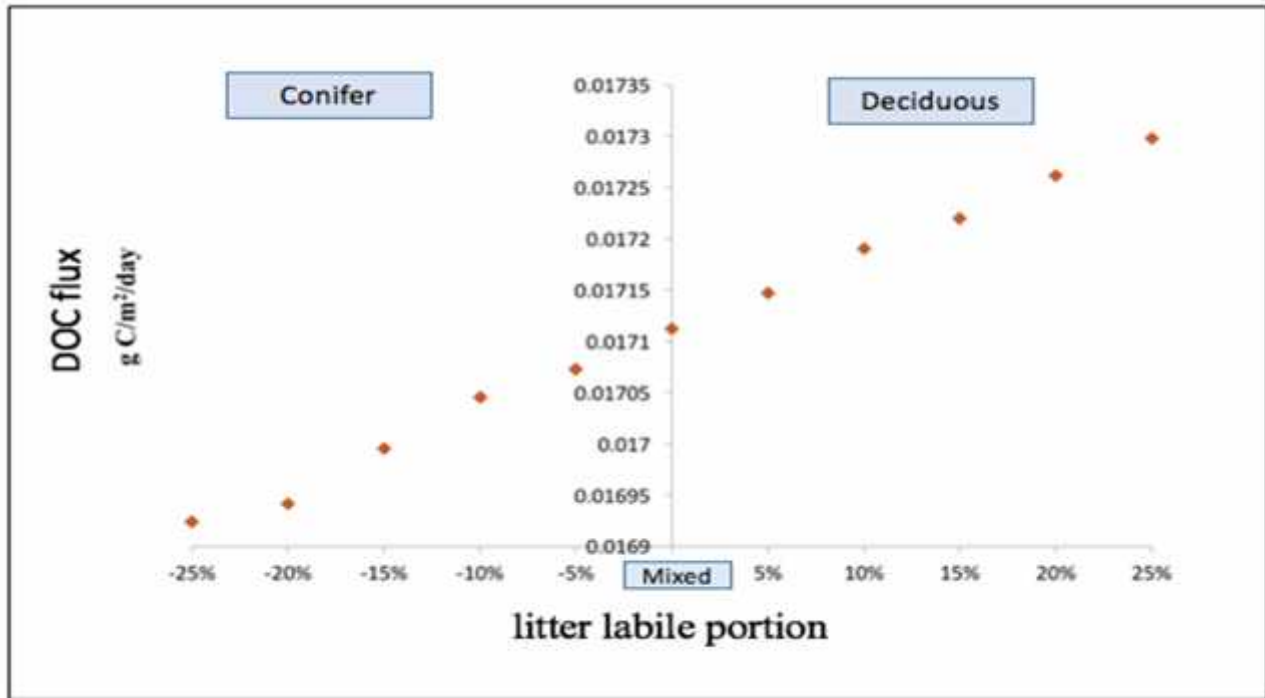


Figure 4.9, Daily streamwater DOC with changes in litter labile portion

4.2.2. Wetland reduction scenario and DOC fluxes

The RHESSys Model utilizes the TOPMODEL approach to model soil moisture redistribution and runoff production. To model saturated subsurface throughflow and overland flow, an explicit routing model is adapted from DHSVM (Wigmosta et al., 1994).

In RHESSys, a parameter defines the wetness status at the patch level (smallest scale in RHESSys, more information can be found in chapter one). The value for each patch is assigned from the input Wetness Index map created from the Digital Elevation Map (DEM). In this study, the Wetness Index Map is calculated from a 30-m DEM which was resampled to 500m. 500m resolution in this study was used due to large size of Penobscot Watershed and the ability of validating our modeled results with MODIS satellite products such as NPP and LAI.

The assigned wetness index value is used for the Local saturation deficit (S_i) calculation for each patch and is defined as:

$$S_i = S + m (W - W_i) \quad (\text{Equation 4.1})$$

Where, (S) is the mean hillslope saturation deficit (considering drainage from unsaturated zone, capillary rise and infiltration along with evapotranspiration from unsaturated zone), and (m) describes a decay rate of hydraulic conductivity with saturation deficit (considering exponential decay), (W) is the mean hillslope wetness index value (from the wetness index map) and (W_i) is the local wetness index computed as:

$$W_i = \ln \frac{a \cdot T}{T_0 \cdot \tan \beta} \quad (\text{Equation 4.2})$$

Where (T_e) and (T_0) are the mean and local hillslope saturated transmissivity respectively, $\tan \beta$ is the local slope, and (a) is the upslope contributing area.

Wetlands are generally located in poorly drained areas at lower elevations with negligible slopes and higher moisture content (higher wetness values) as compared with their surroundings. Figures 4.10 and 4.11, show the Penobscot Watershed wetness map and wetland areas.

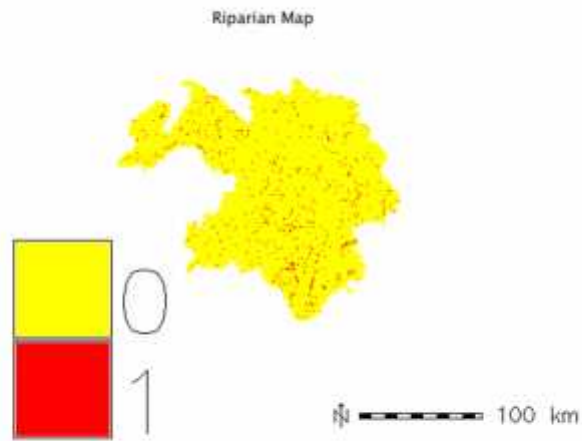


Figure4.10, Penobscot Watershed's Wetlands (0: non wetland and 1: Wetlands)

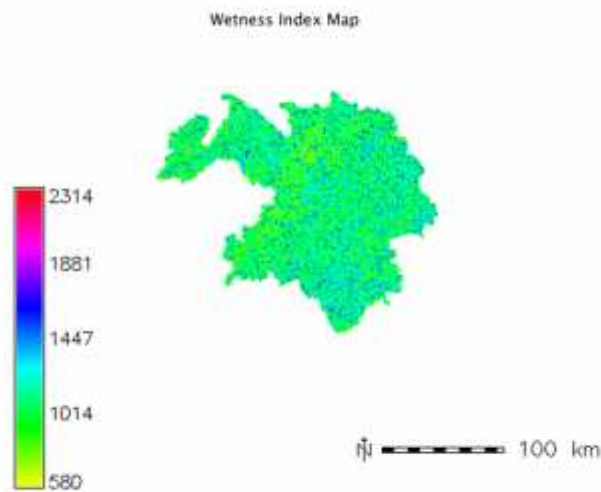


Figure 4.11. Wetness Index MAP calculated from the 30 m DEM map and resampled to 500m

To study the role and importance of wetlands in fluvial DOC export. We also did a sensitivity analysis to see how changing the wetness status would impact the amount of streamflow DOC flux in combination with wetland reduction scenarios. Incremental decreases of 10, 20, 30, 40 and 50 percent reduction in wetland status were considered.

Climate change is expected to impact wetland extent or the extent of inundated areas (Riley et al., 2011, Meng et al., 2012). As an increase in temperature is predicted, we would expect drier peat land areas where wetlands are currently typically located. Moisture influences the decomposition rate of organic matter in the soil as well as water availability for vegetation growth and for transporting DOC from the soil into the stream. We performed an incremental decrease in wetland areas across Penobscot Watershed (5 to 50 percent decline, at 5% intervals).

Thus, in summary, the role of wetlands on the fluvial export of DOC from Penobscot Watershed into the Gulf of Maine was explored by shrinking wetland abundance based on the input wetland map created from reclassified USGS land cover map. As mentioned, approximately 60% of State of Maine Wetlands are forested and the remaining proportion is comprised of shrub, emergent vegetation, or are un-vegetated. In this research, we focused on shrinking the second category containing shrub, emergent vegetation, or un-vegetated areas. In order to shrink wetland areas by 5%-50% , we used spatially balanced points tool in Arc GIS. This tool generates a set of sample points based on inclusion probabilities, resulting in a spatially balanced sample design. Therefore, several wetland maps were created and used as input in the model. Spatially balanced designs, in particular, are constructed to improve the efficiency of estimated values by maximizing spatial independence among sample locations and the samples were selected equally across the Penobscot Watershed (Theobald et al., 2007).

4.3. Results

4.3.1. Impact of forest land cover change on DOC flux and concentrations

With careful parameterization of the spatial-temporal Eco-hydrologic model RHESSys and sensitivity analyses of the various input parameters, we were able to investigate the role of potential shifts in forest vegetation land cover on streamflow DOC flux in the Penobscot Watershed.

Net Primary production (NPP - the amount of carbon uptake after subtracting plant respiration and growth) exerts a major control on the amount of terrestrial DOC export and therefore the accurate quantification of Gross Primary Production (GPP) and NPP are key in modeling the carbon cycle of an ecosystem. Figure 4.12 shows the comparison between the NPP simulated by the RHESSys model and the NPP as derived from MODIS satellite product in deciduous forest. The NPP values for the simulated RHESSys model and the MODIS product cover the same period of time (2004-2013). Our modeled NPP is somewhat higher (ranging from 650-850 g/m²/year) than that estimated from MODIS (ranging from 600-720 g/m²/year).

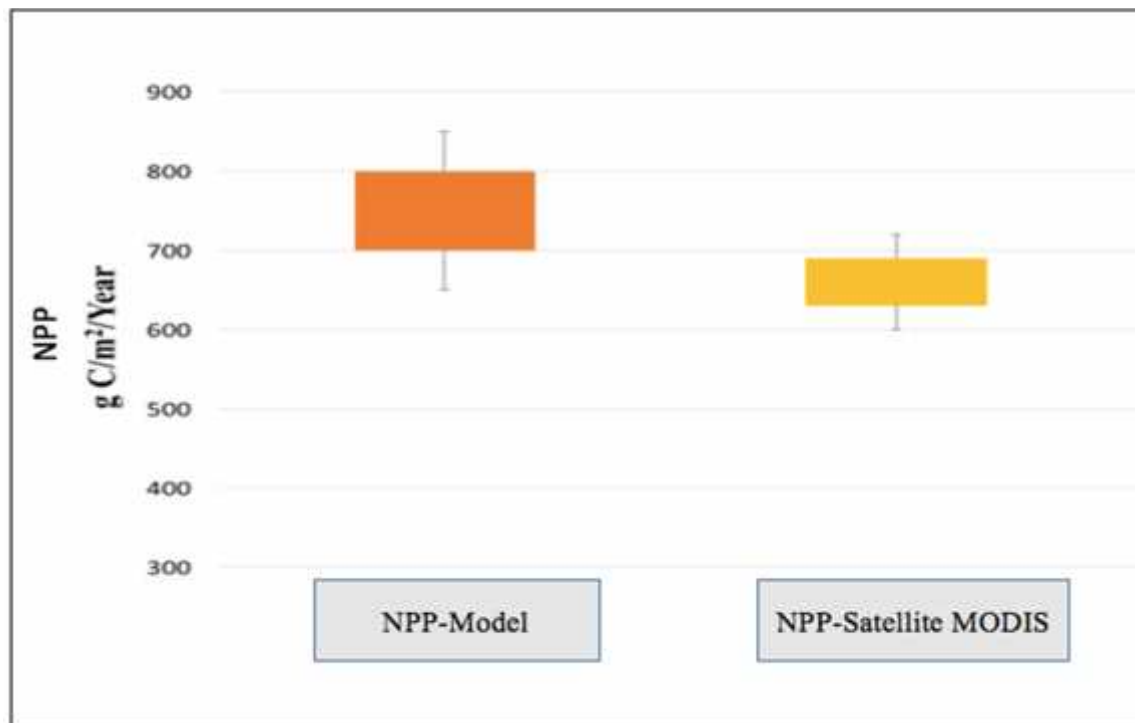


Figure 4.12, Average annual deciduous NPP comparison

We then compared the annual NPP rate from conifers forests from the model results with the MODIS satellite product. Figure 4.12 shows the comparisons between the NPP simulate by the RHESSys model and the NPP from derived from MODIS satellite product for conifer forests. The NPP values for the simulated RHESSys results and the MODIS product cover the same period of time (2004-2013). Our modeled NPP is somewhat higher (ranging from 570-730 g/m²/year) than that estimated from MODIS (ranging from 550-650 g/m²/year).

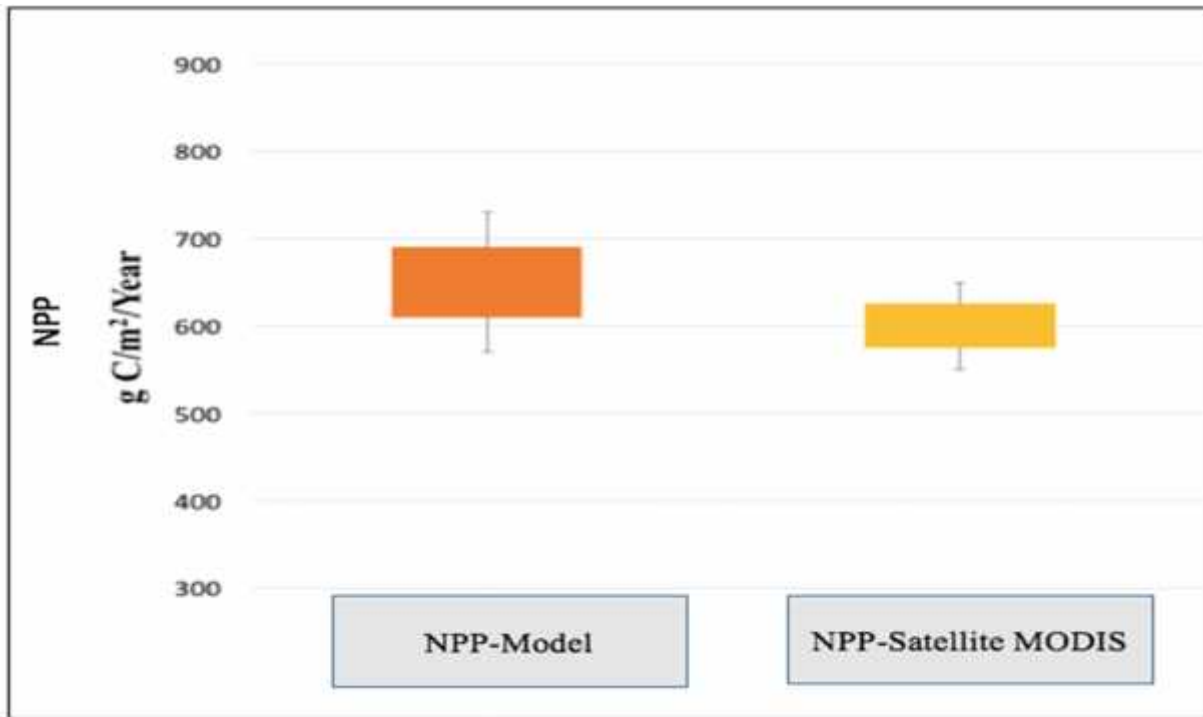


Figure 4.13, Average annual conifer NPP comparison

Overall our modeled NPP is generally lower for the conifer dominant forest than for the deciduous dominant forest, in agreement with previous studies (Ryan et al., 1997; Gower et al., 2001, Brown et al., 1999). The results from the sensitivity analyses performed in this research demonstrate that the higher leaf C:N ratio of conifer trees, along with lower LAI values, will lead to lower NPP values than those associated with deciduous forests.

In order to explore the potential impact of forest species composition change in the future, we have considered four progressive cases to encompass both conifer dominance and deciduous dominance in the State of Maine. Figure 4.14, shows the percentage change in the amount of NPP occurring under various forest vegetation composition changes. The first case is the conversion of the original forest types (mixed, deciduous and conifer) to a combination of conifer (C, 79.7%) and mixed forest (M, 29.3%). The second case is 100% conifer forest. Under

the third case, forest types consist of deciduous (D,68.7%) and mixed forests (M,31.3%), while the fourth case is 100% deciduous forest. Our modeled results indicate that under the first and second cases, going toward conifer dominance forest types, 1.8% and 2.1% declines in the amount of forest net productivity can be expected respectively. While a very slight decrease (-0.2%) in amount of NPP under a total deciduous forest is predicted from our modeled results, an increase of almost one percent is simulated under the third case that consists of a mixture of mixed and deciduous forests.

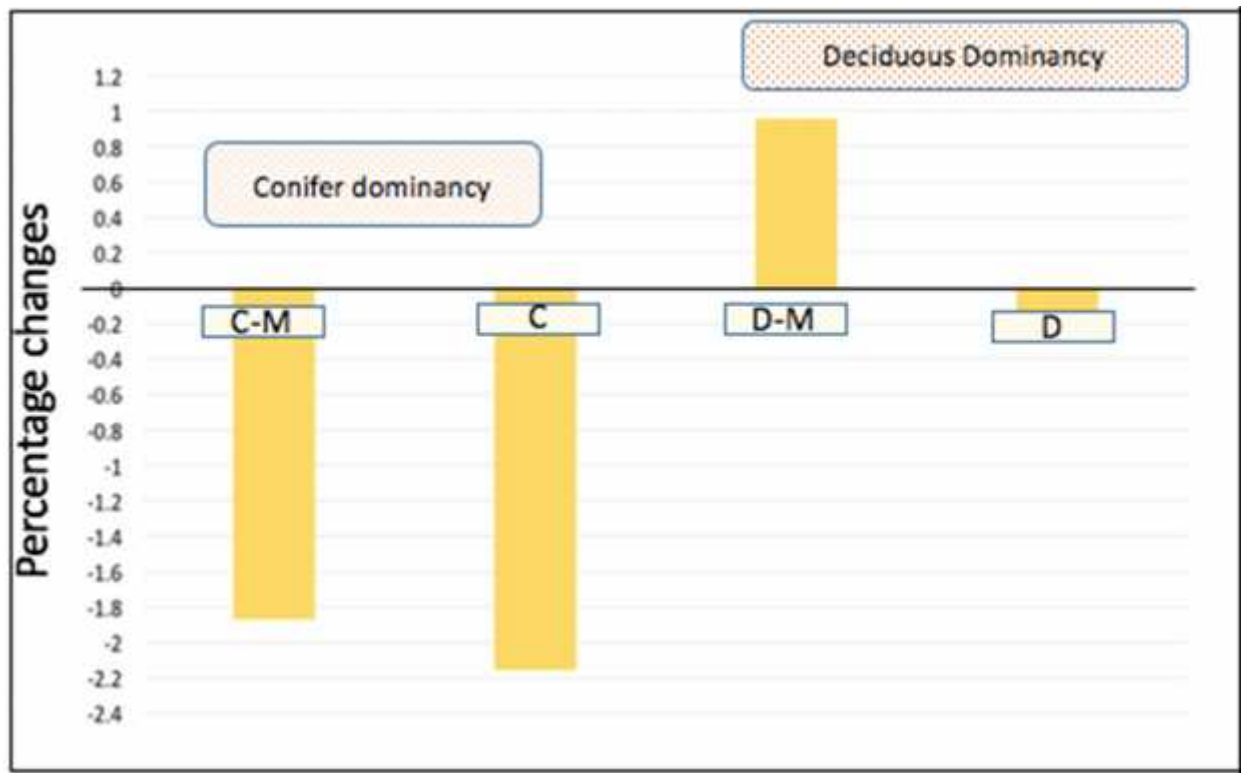


Figure 4.14, Simulated Net Primary production changes based on forest land cover change scenarios

Both our sensitivity analyses described earlier in this chapter and our modeled results of the amount of annual NPP associated with conifer forests support our predicted simulate decline in NPP rates under the conifer dominance cases. Furthermore, according to our sensitivity analyses, a slight decrease under the fourth scenario (100% deciduous) can be attributed to a

plant's component C:N ratios which indicate a potential water limitation situation occurring under a deciduous dominance scenario with a higher LAI. In addition, the NPP slightly increased when the leaf C:N ratio decreased from optimum value for mixed forest to -15%, then decreased slightly with progressive decreases in leaf C:N ratio (representing a simulated deciduous leaf C:N ratio).

The stream DOC simulation has been shown to be largely influenced by the hydrological cycle. There is a strong correlation between the streamflow and the leaching of Dissolved Organic Carbon from the soil (correlation: 0.84, it should be noted that DOC flux is a function of streamflow) and also from the average annual precipitation and the DOC fluxes (correlation: 0.87), as well as from the baseflow and DOC flux (correlation: 0.85). The baseflow (the sustained flow in a channel due to subsurface runoff) is usually higher in deciduous forests than in conifer forests. This results in the higher transport of DOC from the soil to the stream. Conversely there is a negative correlation between annual evapotranspiration and DOC fluxes reported in the sub-streams of the watershed. In addition to a difference between the total amount of evapotranspiration, there is a seasonal variability in the amount of evapotranspiration associated with conifer and deciduous forests. For instance, in winter, evaporation and interception is larger in coniferous forests than in deciduous forests, while deciduous trees generally exhibit reduced transpiration and respiration during drought and dormant seasons. Furthermore, a higher throughfall from deciduous trees (lower interception capacity and shedded leaves during dormant season) can added to increased ground moisture that will directly and positively impact the fluvial DOC export.

A study done by Neary and Gizyn (1994) showed that throughfall directly and positively impact the fluvial DOC export.

A study done by Neary and Gizyn (1994) showed that throughfall was comprised of 74% and 84%, respectively, of the hydrologic flux at a coniferous and a deciduous site. Kirby (1991) and Bosch (1982) reported an annual decrease of 29mm to 40mm in water yield per 10% conifer forest cover.

We then explored the impact of our four progressive forest composition changes on the hydrological cycle as the controlling parameter of streamflow DOC flux and concentration. Figure 4.15 illustrates the impact of forest composition change on the hydrological cycle (streamflow, baseflow and evapotranspiration). Our modeled results showed that, while the amount of baseflow doesn't change for the first (conifer and mixed forest) and second scenarios (total conifer forest), an increase in the evapotranspiration rate and a decrease in streamflow was observed (a 2.5 % and 3% increase in the evapotranspiration rate and a -2.5% and -3.5% decrease in streamflow) were observed from the first and second cases (toward conifer dominance) respectively. In addition, a significant decline in evapotranspiration rates and increases in both the baseflow and streamflow are reported for the third (deciduous and mixed forest) and fourth forest (total deciduous forest) vegetation composition changes. An increase of 5.4% in streamflow and 6% in baseflow, along with a decline of -8% for the evapotranspiration rate, is predicted for the third case (mixed and deciduous forests). In addition, an increase of 8% in streamflow and 7% in baseflow, along with a decline of -12% for the evapotranspiration rate, is predicted for the fourth case (total deciduous forests).

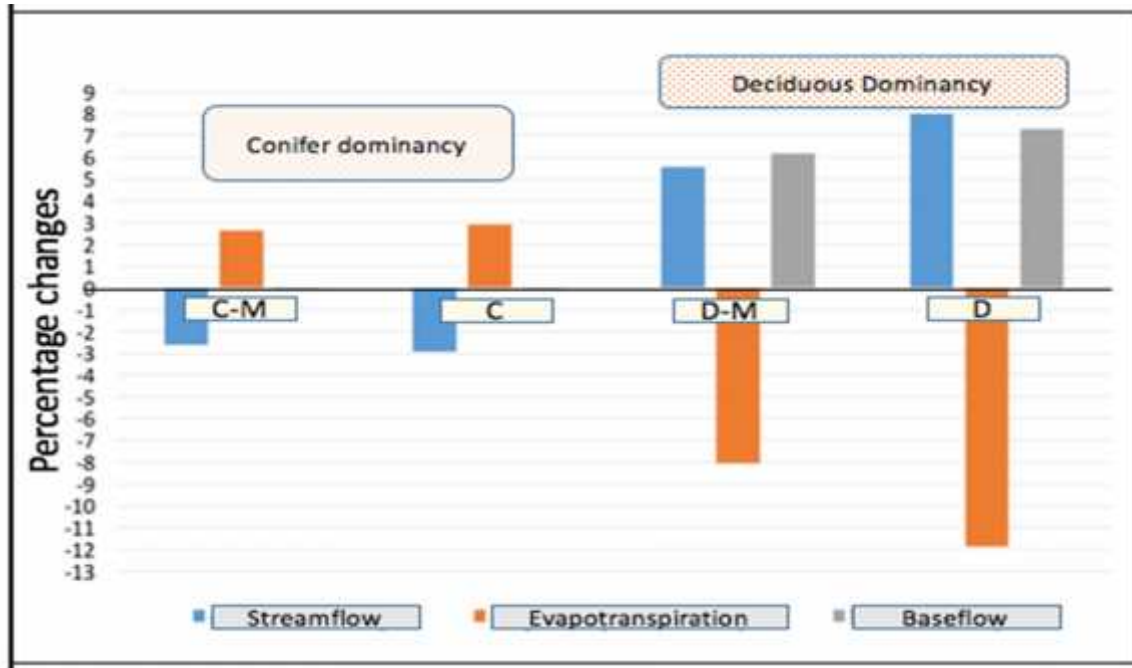


Figure 4.15, the impact of forest land cover change on hydrological cycles (in percentage)

After exploring the impact of these four forest composition changes on NPP and the hydrological cycles, we then investigated the role of forest composition on the amount of streamflow DOC flux. Figure 4.16 shows the percent change in streamflow DOC flux for all four forest composition cases, as well as for DOC concentration. Our simulated results showed a decrease in both DOC flux and DOC concentration under the first (mixed and conifer forests) and second (conifer) cases. Overall a decrease of 5-6 percent in annual streamflow DOC flux and a 3.5-4.6 percent in annual DOC concentration were observed under the first and second cases respectively. While a decrease in both DOC concentration and DOC flux is predicted under cases tending towards conifer dominance, an increase of 1-3 percent in DOC flux and DOC concentration is modeled for the third case (mixed and deciduous forests). Under the total deciduous dominated forest, a slight decrease (-0.5%) in streamflow DOC flux and a 1.5% increase in DOC concentration may be explained by water limitations experienced under total

deciduous forests that was mentioned earlier. This is in agreement with Aitkenhead and McDowell (2000), who also studied the average DOC flux for major biomes in northern temperate latitudes. Their study showed that the average DOC flux from northern mixed forests is the highest, followed by deciduous forests (Table 4.3).

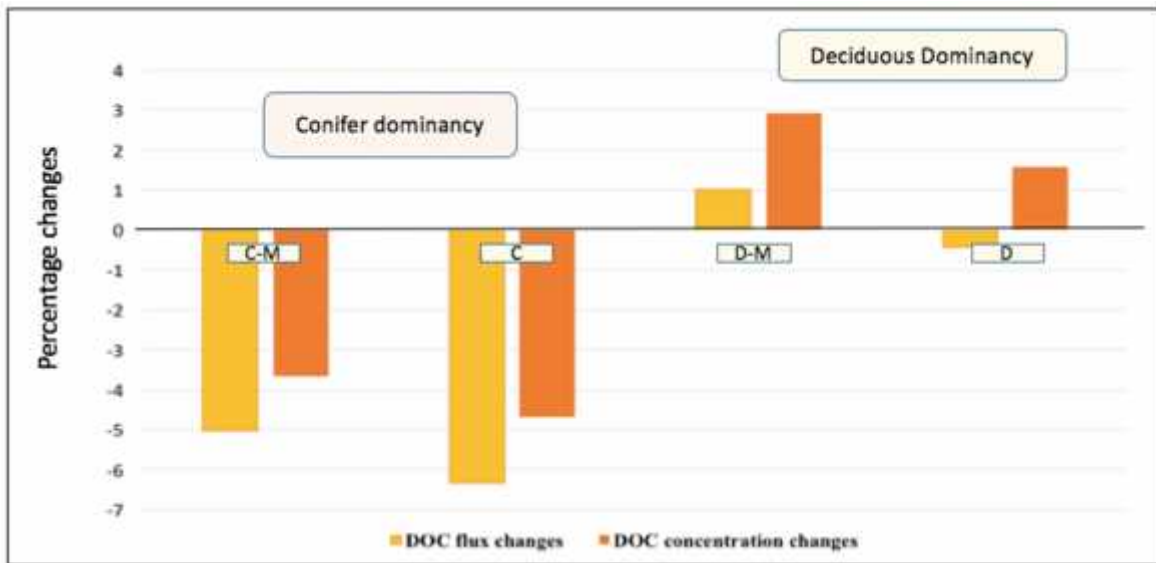


Figure 4.16, The impact of forest land cover change on DOC flux and concentration (in percentages)

Table4.3, Comparison between DOC flux

Biomes or river	DOC flux (Kg C/Ha/year)	Number of catchments	Catchment size (km2)
Cool Conifer Forests (a)	20	30	0.41-830,000
Cool Deciduous forests (a)	42	6	0.13-62.7
Northern mixed forests (a)	53	45	0.1-20,000
Penobscot River (b)	72	1	20,107
Penobscot River (c)	69		
a) Aitkenhead and MCDowell (2000)			
b) Huntington and Aiken (2013)			
c) This study (average annual 2004-2012)			

Seasonal changes were also investigated in order to have a better understanding of the intra-annual variability of streamflow DOC flux and concentration under the changing scenarios. Figure 4.17 illustrates the average percentage seasonal streamflow DOC flux and the concentration change under the various forest land cover change scenarios.

Decline of winter streamflow DOC flux and concentration is shown under all scenarios. The rate of decline in both the DOC flux and DOC concentration is higher under the first (Mixed and conifer forest) and second (conifer forest) cases tending towards conifer dominance. 3.5-4.1 percent decline in DOC flux and 3.2-4 percent decline in DOC concentration is predicted for first and second cases respectively. Our modeled results, showed less of a decline under the third (mixed and deciduous forests) and fourth (deciduous forest) cases. A 1.5- 3percent decline in DOC flux and a 0.5-1.5 percent decline in DOC concentration is predicted for the third and fourth cases respectively.

While there is still a decrease in the amount of DOC flux and concentration under the first and second scenarios (tending towards conifer dominance), an increase in both DOC flux and concentration is predicted for the third and fourth scenarios (tending towards deciduous dominance) in spring time. This can be explained by the higher predicted streamflow, baseflow, and NPP under these scenarios. A 8.5-10.1 percent decline in DOC flux and a 8.4-10 percent decline in DOC concentration is predicted for the first and second cases respectively. The springtime DOC concentration is predicted to have a higher increase (10 percent) under the fourth case (deciduous forest) than the third case (7.5 percent, mixed and deciduous forest), DOC flux is predicted to be lower under fourth case (2 percent) than third case (3.5 percent). This can be explained by the existence of water limitations under a total deciduous forest that results in lower DOC export.

The highest increase in both DOC flux and DOC concentration is expected in the summer time under the third and fourth scenarios when a decline in evapotranspiration rate (deciduous forests interception capacity is lower than conifer and overall they transpire less because of their dormant season), an increase in streamflow and baseflow, and an increase in NPP is expected under the deciduous dominant scenario. Our modeled results showed an increase of 7-11 percent in the DOC flux and 10-18 percent in the DOC concentration under the third (mixed and deciduous forests) and fourth (deciduous forest) scenarios respectively. A 5-7 percent decline in summer time DOC flux and a 3-4 percent decline in summer time DOC concentration under the first (mixed and conifer forests) and second (conifer forest) scenarios respectively, can be explained by a high rate of evapotranspiration under a conifer dominant forest.

A decline in the autumn DOC flux and DOC concentration under the deciduous dominant cases (third and fourth scenarios) also can be explained by the start of leaf off and dormant season for deciduous forests.

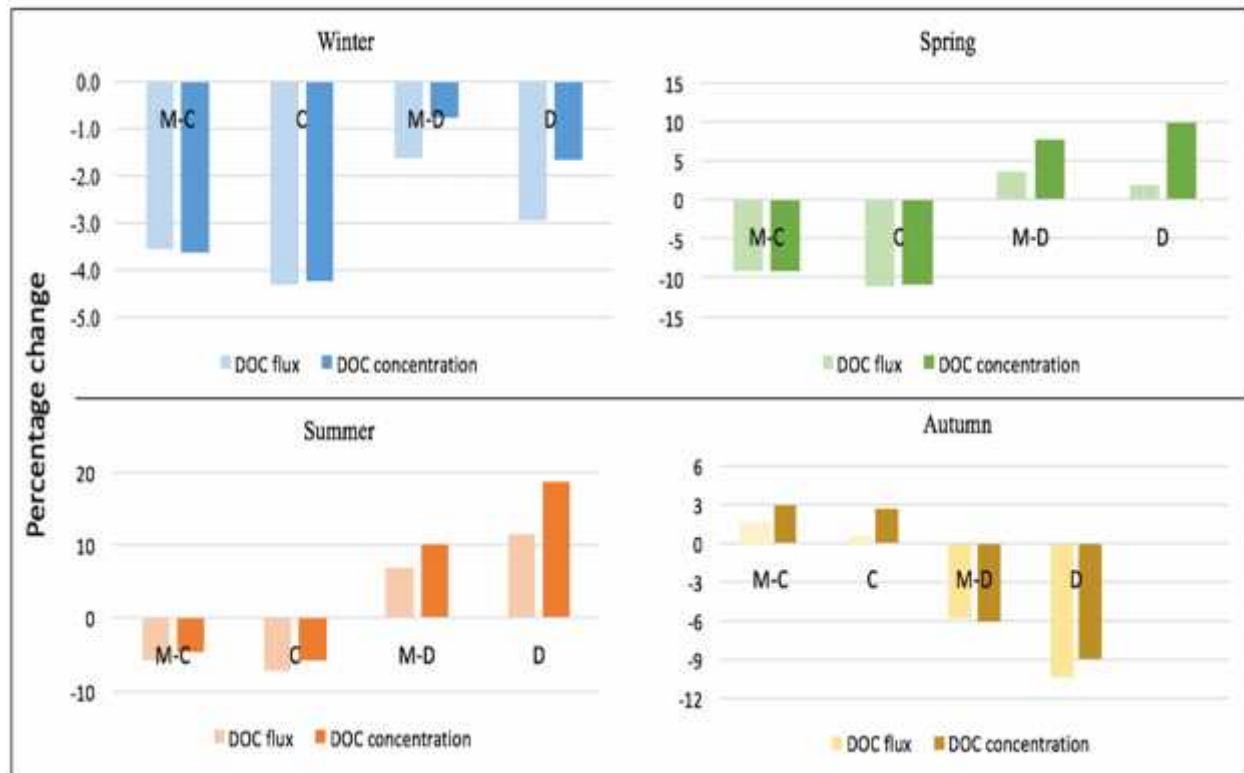


Figure 4.17, The impact of forest land cover change on seasonal DOC flux and concentration (In percentage)

4.3.2. Impact of wetland loss scenarios on DOC flux

The faster growth rate (higher NPP and litter production), higher soil organic matter content, slower rate of decomposition, and the unique hydrological condition of wetlands make this ecosystem a very important source of DOC within a watershed. The high hydrological connectivity of wetlands to river channels can leach DOC out from the land into the river more

effectively than from upland soils that are less hydrologically connected. As discussed earlier in this chapter, the soils of wetlands are well saturated, with poor drainage and a high water table. Streamwater DOC amounts vary by watershed geographic location and topography, climate, soil type, vegetation type, and most importantly, wetland area. The importance of wetland and water yield on DOC concentrations in the Penobscot Watershed in Maine has been previously investigated by Huntington and Aiken (2013).

A sensitivity analysis on the wetness status of reduced wetland area was explored in this study. Figure 4.18 shows the results from simulated changes in wetness status and the impacts on streamflow DOC. Our simulated results didn't show a significant response to changes in wetness status (for a 50% decrease in wetness status, there was only a -0.06% change in average daily streamwater DOC).

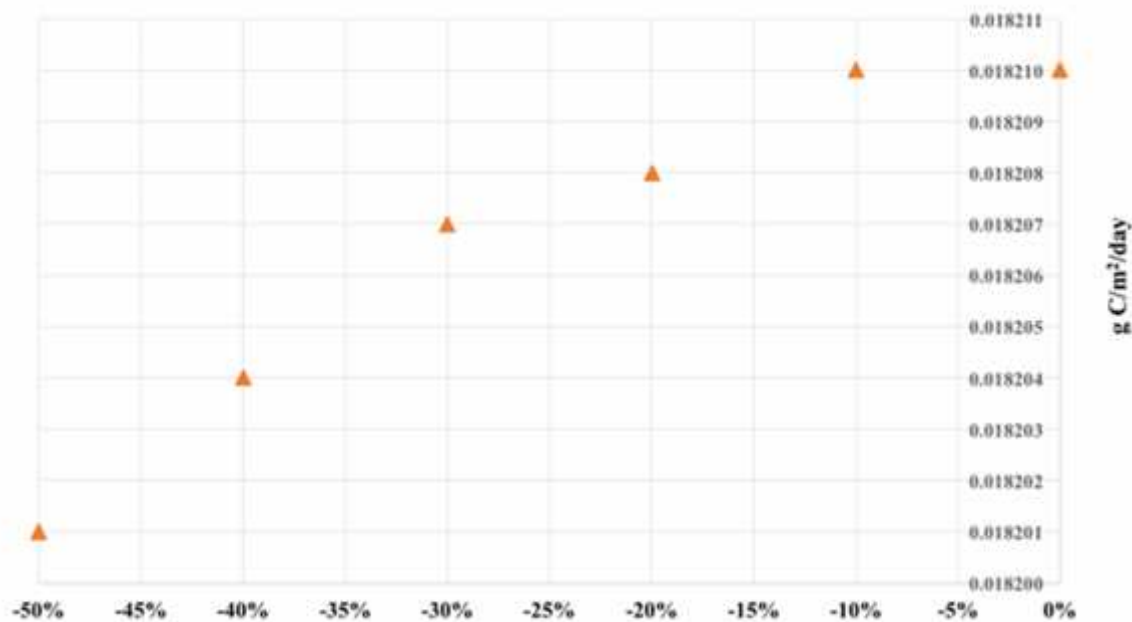


Figure 4.18, Average daily streamwater DOC changes by changes in wetness status

Therefore, in this study, we explored changes in streamflow DOC flux under two scenarios of gradual wetland loss. In our first scenario, we decreased the extent of wetlands by 5%-50% and converted the wetlands to grasslands. In our second scenario, we converted the wetlands to un-vegetated areas. Figure 4.19 shows the impact of wetland change into grassland (Blue) and of wetland change into un-vegetated areas (Orange) on the annual DOC flux. The results are presented in percentage change. Our simulated results suggest that even a 50% percent decline in scrub-shrub wetlands and a transformation of the emergent wetlands into grasslands would not result in substantial changes in streamflow DOC flux (-0.15 percent). Our RHESSys model didn't show much sensitivity to changes in wetness status and contribute to our underestimation of the impact of wetlands under this scenario. However, the streamflow DOC flux changes in response to changes of incremental wetland loss and transformation to un-vegetated areas, resulted in a higher decrease. With a 50% reduction in wetland area, a 1.7% decrease in streamflow DOC flux was predicted.

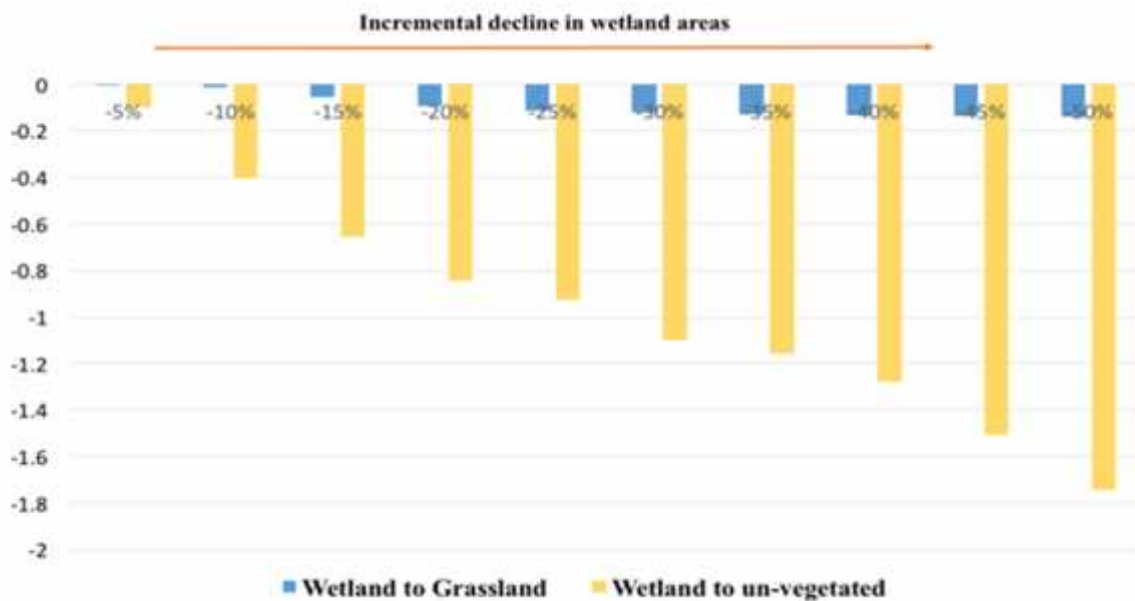


Figure 4.19, The impact of wetland loss scenarios on annual DOC flux (in percentage)

The response of streamflow DOC flux to future climate projections was studied and discussed earlier (chapter three), but here we studied the impact of both wetland loss and a future climate change scenario (The mean scenario under low emissions for the *mid century*) on streamflow DOC flux. Figure 4.20 represents the combined impact of wetland loss scenarios and climate projections on the annual DOC flux. Our results indicate that the impact of mixing both a wetland loss scenario with a future climate change scenario (a mean scenario under low emission for *mid-century*) shows less of an increase in streamflow DOC flux than compared to a future climate scenario alone (a 7% increase, presented in chapter three, figure 3.8).

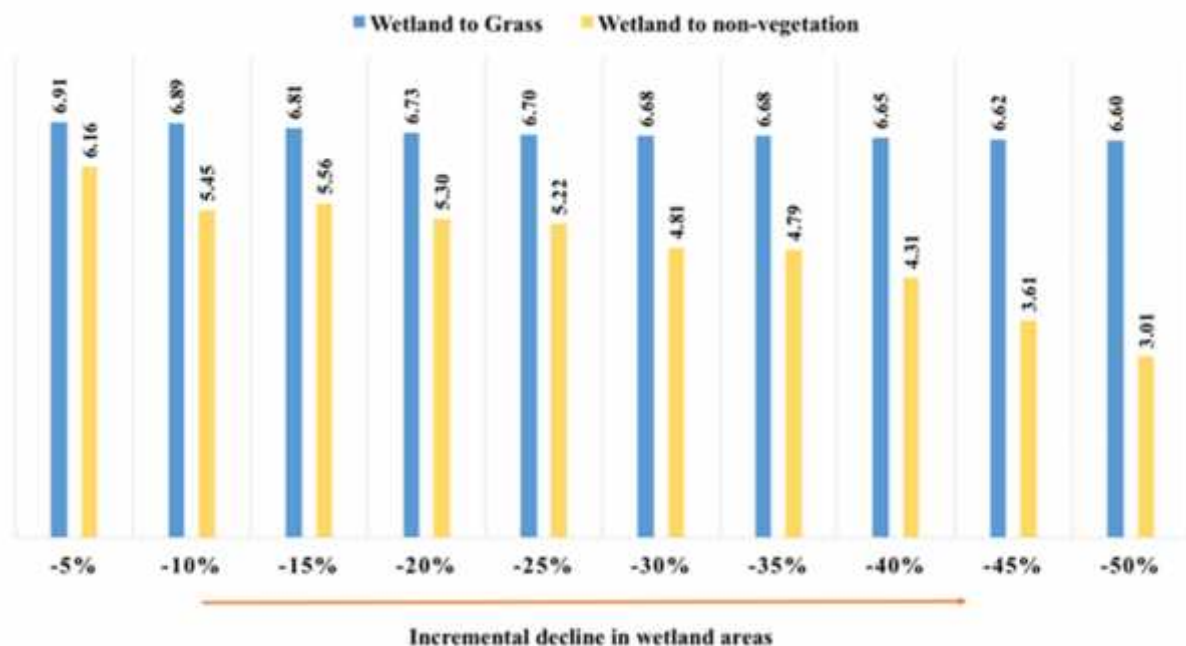


Figure 4.20, The combined impact of wetland loss scenarios and climate projections on annual DOC flux (in percentage)

In our second approach to exploring the role of wetland loss in the Penobscot Watershed, we performed an explicit strategy, where Arc GIS tools were used to shrink the wetland area and convert it to upland landcovers. We shrank the wetland areas across Penobscot Watershed by one (500m) pixel and then by two pixels. Table 4.4 illustrates the changes that occur in the Penobscot Watershed's vegetation types when shrinking wetland areas by first one pixel (Shrink_1) and then by two pixels (shrink_2). The changes are shown in percentage. The highest conversion of wetlands is predicted to be to mixed forest.

Table4.4, The Penobscot Watershed's vegetation types changes by shrinking wetland areas

Vegetation	Original(%)	Shrink_1(%)	Shrink_2(%)
Wetland	8.5	5.53	3.23
Mixed forest	31.89	35.24	37.42
Crop	1.3	1.45	1.74
Grass	13.48	15.02	15.53
Deciduous	13.38	14.16	15.23
Conifer	20.68	22.85	24.1
Shrub	3.63	4.08	4.75

Figure 4.21 presents the average annual DOC flux changes under the wetland loss scenarios. The one-pixel shrink resulted in a loss of approximately 40% of the wetland area and a two pixels shrink resulted in a loss of 62% of the wetland area. Our modeled results indicated that a 40% decrease in wetland area resulted in a decrease of 1.2 percent in the average annual DOC flux and a 62% decrease in the wetland area resulted in a decrease of 2.1 percent in the average annual DOC flux.

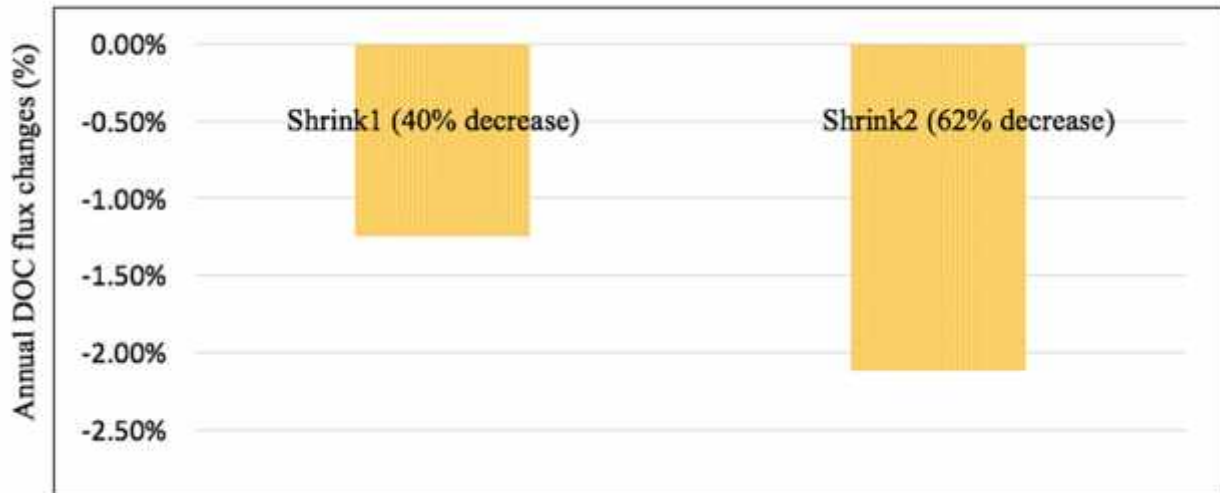


Figure 4.21, Average annual DOC flux change under wetland loss scenarios

4.4. Conclusions

In large, more heterogeneous catchments, like the Penobscot, the streamflow dissolved organic carbon (DOC) dynamics are regulated by the combined effect of hydrological mechanisms and the proportions of the major landscape elements in the watershed (in this case, wetlands and forested areas).

DOC production is a function of the net primary production (NPP) and the organic matter decay, which are also affected by environmental variables (precipitation and temperature) as well as by soil water content. Our results indicated that deciduous forests are usually characterized by higher NPP, streamflow, baseflow and lower evapotranspiration rate than conifer forest, and they are strongly correlated with streamflow DOC flux.

The simulated results suggest a decrease of 5%-6% in the annual streamflow DOC flux under cases where the original forest vegetation composition was changed to conifer dominant forests. Intra-annual phenological changes may possibly explain some portion of the inter-annual pattern seen, as different vegetation types display different sensitivities to the allocation and the

timing of phenology. For instance, conifers tend to be less sensitive to phenological timing because they experience only a minor loss of needles, while deciduous trees are typically more sensitive as they need to have a specific allocation strategy to restart photosynthesis during the spring.

A number of studies have demonstrated that the amount of wetlands, especially peatlands, will control the watershed level transport of DOC in streams. Wetlands are known to have a high turnover rate of leaves and a high rate of decomposition of organic matter, as well as a high hydrologic conductivity, which allows DOC to leach out of the land into the stream. Our modeled results didn't show a sensitivity to changes in the wetness status, which suggest that our model results may somewhat overestimate the role of hydrologic dynamics in a wetland's soil profile when changing that wetlands to grassland. So, our simulated DOC fluxes may be larger than expected under wetland loss scenarios.

Furthermore, our simulated results show that the projected loss of wetland to un-vegetated areas would decrease the magnitude of any increased DOC flux in the future that would expected due to future climate projections. Therefore, as a result of expected changes due to future land cover change and climate trends, DOC will continue to serve as an important response variable in a full understanding of carbon storage and fluxes. Study of various forest vegetation composition changes and of wetland loss scenarios have greatly expanded our understanding of the role of vegetation type (conifer, deciduous and wetlands) on Net Primary Production and on the streamflow DOC flux. However, further consideration still needs to be given to the complex role of wetlands as carbon sources, and sinks.

CHAPTER 5

SUMMARY

This research incorporated a spatially distributed, hydro-ecologic process based model (RHESSys) and remotely sensed data to simulate detailed forest and wetland processes in the second largest watershed in New England. The results were evaluated by comparison with field data and other model results. The impact of future changes (of climate and of land cover) on the annual and seasonal peak DOC discharge, as well as on the the timing of these peaks and related shifts in the timing of snowmelt were explored in this research.

Given the ongoing changes in land cover and climate (and those expected in the future), the study of response variables such as DOC flux and snowmelt timing are critical to document the significant components of the terrestrial carbon budget and water supply respectively. The RHESSys model was initialized and validated with both remotely sensed data (NPP and LAI products) and *in situ* measurements (streamflow and DOC flux) thereby providing a reliable platform to explore both ecological and hydrological controls on DOC flux and concentration in this large-heterogeneous watershed. Furthermore, dynamic coupling between the hydrologic response and possible land cover changes and vegetation dynamics in the RHESSys model makes our study of the impact of future projections more realistic.

A set of sensitivity analyses on the RHESSys simulated DOC flux and Net Primary Production were also undertaken in this study to explore both the hydrological and ecological processes affecting terrestrial DOC leach out. The impact of vegetation specific physiological parameters, such as the ratio of carbon to nitrogen in leaves, roots, and litter, as well as the impact of litter quality and LAI, on the NPP and DOC flux were also investigated during this research to understand the ecological control of plants on the production of DOC. Similarly, the impact of streamflow, baseflow, and evapotranspiration was used to explore the hydrological controls on DOC leach out.

In addition, two different methodologies to partition winter time precipitation (the original RHESSys methodology and the Dingman et al., 2014 methodology) were used during this study to investigate possible improvements in our ability to study temporal changes in the timing of snowmelt.

Using various remotely sensed data and daily climate inputs (minimum, maximum temperature and precipitation), we were able to successfully simulate the streamflow and DOC flux and concentration in our research area. Note that this implementation of RHESSys in the Penobscot Watershed represents the largest implementation of RHESSys yet attempted, and numerous logistical difficulties, due to the sheer size of the watershed, needed to be overcome.

The Streamflow Center Timing (CT) approach was used to study the temporal trends in the Winter-Spring (January 1st-May 31st) streamflow as an indicator of any shifts in snowmelt timing. Since, our simulated Winter-Spring Center Timing results for the period of 2004-2013 corresponded very well with the observed values, we expanded our study to detect any possible changes in the timing of snowmelt based on the *mean* and *very likely* future climate projections under both the low and high emission *scenarios* for both the *mid-* and *end-of-the-century* time

periods. In addition to studying the impact of combined temperature and precipitation changes, we also evaluated the sensitivity of these projected shifts in snowmelt timing to changes temperature and precipitation separately, as they were projected to be the environmental factors most affecting temporal trends in timing of snowmelt.

A significant trend towards earlier snowmelt timing has been detected since 1960. A seven-day shift was estimated for the average decadal interval over the period of 1960-2013 (P-value<0.05). Furthermore, while our simulated results predict a significantly earlier trend for snowmelt under the *mean* (both low and high emission) and the *very likely* (under high emission) scenarios, while a trend toward later dates of snowmelt (P-value > 0.1) was predicted for the *very likely* climate projection under the low emission scenario (a decrease in precipitation is predicted for all seasons under the *very likely*, low emission scenarios).

In addition, our sensitivity simulations revealed a strong correlation between the projected increases in winter-spring temperature and changes in snowmelt timing – more so than the correlations due to future changes in the October through April precipitation. Our simulated results show continuing changes in the form of precipitation (more falling as rain than as snow) in the future, which will also control the timing of snowmelt. These predictions of substantial changes in the timing of snowmelt runoff resulted in a shift of one to three weeks in earlier timing under the different future climate projection scenarios used in this research. These predicted shifts should also be noted by water resources decision makers as these changes may impact water supplies in future.

The simulation also investigated the impact on the amount and timing of DOC flux in the future. RHESSys, as a spatially distributed model that integrates vegetation dynamics, water,

climate, and carbon interactions, allowed for the projection of the impact of climate and land cover changes, and thereby furthered our understanding of terrestrial DOC fluxes in the future.

The RHESSys simulated DOC fluxes corresponded better with the observed values (r : 0.66) than the correlation with the DOC concentrations (0.42). Higher correlations were observed during winter time (r : 0.86) and lower in spring (r : 0.6). Furthermore, in general, our simulated DOC flux result corresponds well with regression modeled values from the LOADEST empirical model.

The successful application of RHESSys for the simulation of DOC flux and concentration in this large forested watershed represents a reliable scheme to test several hypotheses to expand our understanding of both the ecological and hydrological controls on DOC production and fluxes. Future changes in the amount of streamflow DOC were also investigated through the use of future projected land cover and climate change scenarios.

Several sensitivity analyses were also undertaken to evaluate the impact of soil parameters (DOM production rate and DOC absorption), vegetation parameters (leaf, root, and litter C:N ratios and LAI) and climate factors (temperature and precipitation) on the simulated DOC fluxes. The impact of increases in the growing season length on the DOC production and fluxes was also investigated.

The variation in the above factors influenced the DOC eco-hydrological processes by regulating the hydrology and vegetation growth. While slightly higher DOM production rates means that more litter carbon is being converted to DOC, a very high DOM production rate may also cause a nitrogen limited environment, which will eventually impact net primary production and will limit the source of DOC as well as the water required for DOC leach out.

A very careful model parameterization was needed for DOC absorption rates due to the existence of lakes and reservoirs within Penobscot Watershed. Slightly lower DOC absorption rates may result in large increases in streamflow DOC flux. In addition, increases in the length of the growing season alone (without any changes in precipitation) were shown to decrease fluvial DOC export by increasing evapotranspiration and decreasing the soil moisture, hydrological processes thus affecting the DOC flux.

Forest carbon cycling behavior appears to be undergoing an alteration in response to climate projections and land cover changes. Therefore, progressive changes in the extent and species composition of forested land covers were also implemented to understand the role that vegetation in the watershed plays in determining the DOC flux. To understand this role, the impact of the species specific vegetation parameters on NPP, and therefore DOC production and flux, was also explored. Positive correlations between the vegetation NPP, the streamflow, the precipitation, and the baseflow with the terrestrial DOC flux were observed in this study, and a negative correlation between the evapotranspiration and the amount of DOC flux was also detected.

In general, Conifer forests had higher leaf and litter C:N ratios, lower litter labile components, and lower LAIs, all of which resulted in lower NPP. These factors, along with higher evapotranspiration and lower streamflow and baseflow in conifer dominant forests, resulted in less of an annual terrestrial DOC flux than from deciduous forests, with the highest changes occurring in the spring time DOC flux.

The annual export of DOC was found to increase under most projected climate scenarios with the highest increase occurring in the winter time as a result of projected increases in both winter temperature and precipitation. Higher winter precipitation, along with increases in

temperature, resulted in changes in the form of winter precipitation (from snow to rain). The annual peak DOC release is now seen to be almost coinciding with the timing of the snowmelt. Projected shifts in the timing of snowmelt lead to changes in the timing of peak DOC discharge as well. In addition, our results indicate that changes in temperature are better correlated with changes in future streamflow DOC flux than are changes in precipitation.

Future climate change is predicted to change the amount and timing of streamflow as well as the abundance of wetlands and therefore to effect the amount of DOC production and fluxes. Incremental reductions in the extent of wetland area were used to explore the sensitivity of this watershed to wetland loss. This wetland study was undertaken to discern and quantify the eco-hydrologic function of the wetland areas within the Penobscot catchment, focusing on the amount of DOC release. The role of the wetlands under future climate projections was then used to understand future possible changes in carbon storage and flux. Our simulated results indicate that DOC reductions caused by watershed wetland loss may decrease the magnitude of any increased DOC fluxes in the future that would be expected as a result of climate projections.

Most studies on future changes (land cover and climate changes), have just considered the impact on hydrology and have ignored the impact of vegetation dynamics. Vegetation can alter the streamflow regime by affecting evapotranspiration due to shifts in phenology and vegetation composition that will impact their water supply strategy. RHESSys has enhanced our ability to better understand the mechanisms that drive the biogeochemical processes that control the spatiotemporal variability of streamflow DOC within a very large catchment, as well as explore the impact of vegetation processes on streamflow. Thus RHESSys is shown to be able to better capture and illuminate the complex interactions between large scale ecosystem processes that are not readily available from in-situ measurements or from empirical models alone.

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